

Figure 6-2. Sulfur Dioxide Sampling Train Using a Critical Orifice.

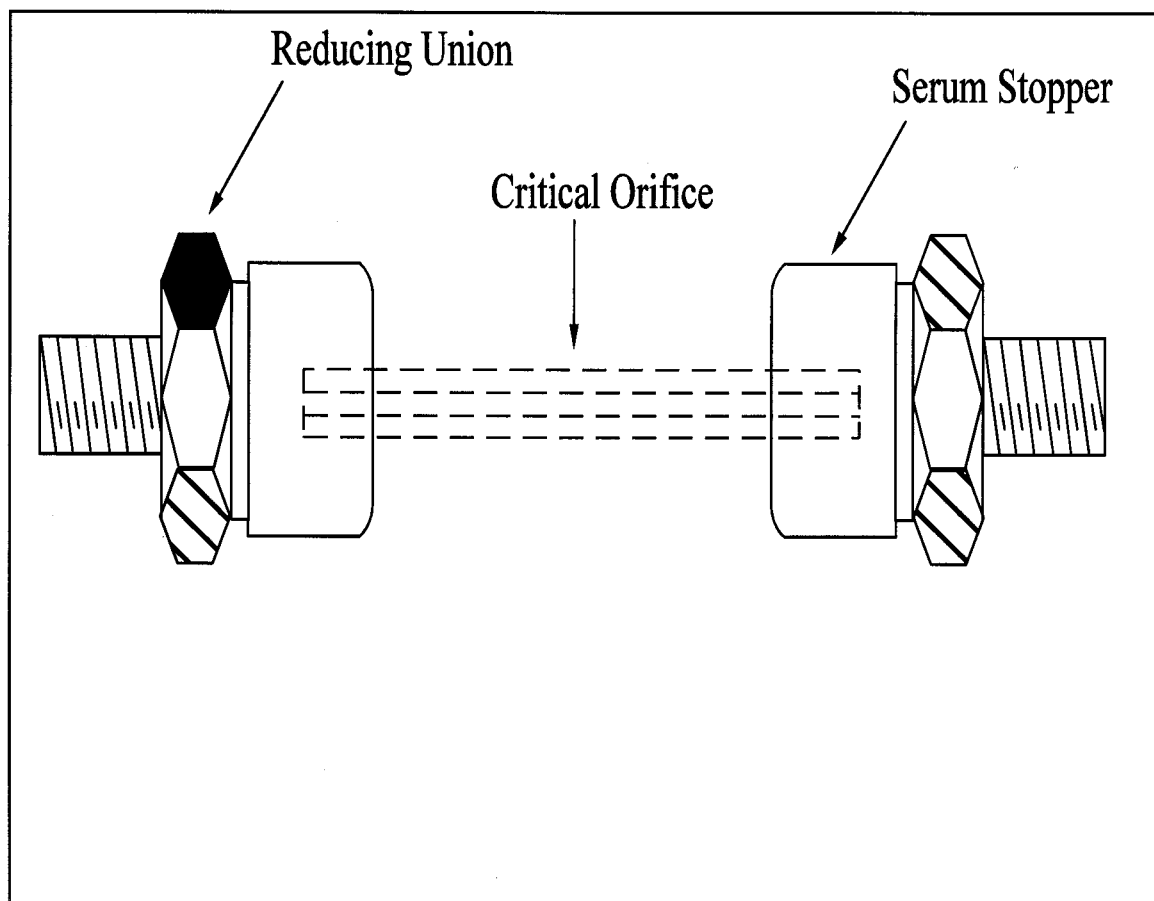


Figure 6-3. Critical Orifice Adaptation for the Method 6 Sampling Train.

Date _____	Train ID _____		
Critical orifice size _____	Critical vacuum _____		
		<u>Pretest</u>	<u>Post-test</u>
Soap bubble meter volume, cc		_____	_____
$V_{sb}$			
	$m^3 (ft^3)$	_____	_____
Time, $\theta$	sec	_____	_____
	min	_____	_____
Barometric pressure, $P_{bar}$	mm Hg (in. Hg)	_____	_____
Ambient temperature, $t_{amb}$	$^{\circ}C (^{\circ}F)$	_____	_____
Inlet vacuum, $P_c$	mm Hg (in. Hg)	_____	_____
Outlet vacuum	mm Hg (in. Hg)	_____	_____
$V_{sb(std)}$	$m^3 (ft^3)$	_____	_____
Flow rate, $Q_{std}$	$\frac{m^3}{min} \left( \frac{ft^3}{min} \right)$	_____	_____

Figure 6-4. Critical Orifice Calibration Data Sheet.

## Method 6A—Determination of Sulfur Dioxide, Moisture, and Carbon Dioxide From Fossil Fuel Combustion Sources

**Note:** This method does not include all of the specifications (e.g., equipment and

supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge

of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, Method 6, and Method 19.

### 1.0 Scope and Application

#### 1.1 Analytes.

Analyte	CAS No.	Sensitivity
SO <sub>2</sub> .....	7449-09-05	3.4 mg SO <sub>2</sub> /m <sup>3</sup> (2.12 × 10 <sup>-7</sup> lb/ft <sup>3</sup> )
CO <sub>2</sub> .....	124-38-9	N/A
H <sub>2</sub> O .....	7732-18-5	N/A

1.2 Applicability. This method is applicable for the determination of sulfur dioxide (SO<sub>2</sub>) emissions from fossil fuel combustion sources in terms of concentration (mg/dscm or lb/dscf) and in terms of emission rate (ng/J or lb/10<sup>6</sup> Btu) and for the determination of carbon dioxide (CO<sub>2</sub>) concentration (percent). Moisture content (percent), if desired, may also be determined by this method.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

### 2.0 Summary of Method

2.1 A gas sample is extracted from a sampling point in the stack. The SO<sub>2</sub> and the sulfur trioxide, including those fractions in any sulfur acid mist, are separated. The SO<sub>2</sub> fraction is measured by the barium-thorin titration method. Moisture and CO<sub>2</sub> fractions are collected in the same sampling train, and are determined gravimetrically.

### 3.0 Definitions. [Reserved]

### 4.0 Interferences

Same as Method 6, Section 4.0.

### 5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. Same as Method 6, Section 5.2.

### 6.0 Equipment and Supplies

6.1 Sample Collection. Same as Method 6, Section 6.1, with the exception of the following:

6.1.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 6A-1.

6.1.1.1 Impingers and Bubbler. Two 30=ml midjet impingers with a 1=mm restricted tip and two 30=ml midjet bubblers with unrestricted tips. Other types of impingers and bubblers (e.g., Mae West for SO<sub>2</sub> collection and rigid cylinders containing Drierite for moisture absorbers), may be used with proper attention to reagent volumes and levels, subject to the approval of the Administrator.

6.1.1.2 CO<sub>2</sub> Absorber. A sealable rigid cylinder or bottle with an inside diameter between 30 and 90 mm, a length between 125 and 250 mm, and appropriate connections at both ends. The filter may be a separate heated unit or may be within the heated portion of the probe. If the filter is within the sampling probe, the filter should not be within 15 cm of the probe inlet or any unheated section of the probe, such as the connection to the first bubbler. The probe and filter should be heated to at least 20 °C (68 °F) above the source temperature, but not greater than 120 °C (248 °F). The filter temperature (i.e., the sample gas temperature) should be monitored to assure the desired temperature is maintained. A heated Teflon connector may be used to connect the filter holder or probe to the first impinger.

**Note:** For applications downstream of wet scrubbers, a heated out-of-stack filter (either borosilicate glass wool or glass fiber mat) is necessary.

6.2 Sample Recovery. Same as Method 6, Section 6.2.

6.3 Sample Analysis. Same as Method 6, Section 6.3, with the addition of a balance to measure within 0.05 g.

### 7.0 Reagents and Standards

**Note:** Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. Where such specifications are not available, use the best available grade.

7.1 Sample Collection. Same as Method 6, Section 7.1, with the addition of the following:

7.1.1 Drierite. Anhydrous calcium sulfate (CaSO<sub>4</sub>) desiccant, 8 mesh, indicating type is recommended.

**Note:** Do not use silica gel or similar desiccant in this application.

7.1.2 CO<sub>2</sub> Absorbing Material. Ascarite II. Sodium hydroxide-coated silica, 8- to 20-mesh.

7.2 Sample Recovery and Analysis. Same as Method 6, Sections 7.2 and 7.3, respectively.

### 8.0 Sample Collection, Preservation, Transport, and Storage

#### 8.1 Preparation of Sampling Train.

8.1.1 Measure 15 ml of 80 percent isopropanol into the first midjet bubbler and 15 ml of 3 percent hydrogen peroxide into each of the two midjet impingers (the second and third vessels in the train) as described in Method 6, Section 8.1. Insert the glass wool into the top of the isopropanol bubbler as shown in Figure 6A-1. Place about 25 g of Drierite into the second midjet bubbler (the fourth vessel in the train). Clean the outside of the bubblers and impingers and allow the vessels to reach room temperature. Weigh the four vessels simultaneously to the nearest 0.1 g, and record this initial weight (m<sub>wi</sub>).

8.1.2 With one end of the CO<sub>2</sub> absorber sealed, place glass wool into the cylinder to a depth of about 1 cm (0.5 in.). Place about 150 g of CO<sub>2</sub> absorbing material in the cylinder on top of the glass wool, and fill the remaining space in the cylinder with glass wool. Assemble the cylinder as shown in Figure 6A-2. With the cylinder in a horizontal position, rotate it around the horizontal axis. The CO<sub>2</sub> absorbing material should remain in position during the rotation, and no open spaces or channels should be formed. If necessary, pack more glass wool into the cylinder to make the CO<sub>2</sub> absorbing material stable. Clean the outside of the cylinder of loose dirt and moisture and allow the cylinder to reach room temperature. Weigh the cylinder to the nearest 0.1 g, and record this initial weight (m<sub>ai</sub>).

8.1.3 Assemble the train as shown in Figure 6A-1. Adjust the probe heater to a temperature sufficient to prevent condensation (see **Note** in Section 6.1). Place crushed ice and water around the impingers and bubblers. Mount the CO<sub>2</sub> absorber outside the water bath in a vertical flow position with the sample gas inlet at the bottom. Flexible tubing (e.g., Tygon) may be used to connect the last SO<sub>2</sub> absorbing impinger to the moisture absorber and to connect the moisture absorber to the CO<sub>2</sub> absorber. A second, smaller CO<sub>2</sub> absorber containing Ascarite II may be added in-line downstream of the primary CO<sub>2</sub> absorber as a breakthrough indicator. Ascarite II turns white when CO<sub>2</sub> is absorbed.

8.2 Sampling Train Leak-Check Procedure and Sample Collection. Same as Method 6, Sections 8.2 and 8.3, respectively.

### 8.3 Sample Recovery.

8.3.1 Moisture Measurement. Disconnect the isopropanol bubbler, the SO<sub>2</sub> impingers, and the moisture absorber from the sample train. Allow about 10 minutes for them to reach room temperature, clean the outside of loose dirt and moisture, and weigh them simultaneously in the same manner as in Section 8.1. Record this final weight (m<sub>wf</sub>).

8.3.2 Peroxide Solution. Discard the contents of the isopropanol bubbler and pour the contents of the midget impingers into a leak-free polyethylene bottle for shipping. Rinse the two

midget impingers and connecting tubes with water, and add the washing to the same storage container.

8.3.3 CO<sub>2</sub> Absorber. Allow the CO<sub>2</sub> absorber to warm to room temperature (about 10 minutes), clean the outside of loose dirt and moisture, and weigh to the nearest 0.1 g in the same manner as in Section 8.1. Record this final weight (m<sub>af</sub>). Discard used Ascarite II material.

### 9.0 Quality Control

Same as Method 6, Section 9.0.

### 10.0 Calibration and Standardization

Same as Method 6, Section 10.0.

### 11.0 Analytical Procedure

11.1 Sample Analysis. The sample analysis procedure for SO<sub>2</sub> is the same as that specified in Method 6, Section 11.0.

11.2 Quality Assurance (QA) Audit Samples. Analysis of QA audit samples is required only when this method is used for compliance determinations. Obtain an audit sample set as directed in Section 7.3.6 of Method 6. Analyze the audit samples, and report the results as directed in Section 11.3 of Method 6. Acceptance criteria for the audit results are the same as those in Method 6.

### 12.0 Data Analysis and Calculations

Same as Method 6, Section 12.0, with the addition of the following:

#### 12.1 Nomenclature.

C<sub>w</sub> = Concentration of moisture, percent.

C<sub>CO2</sub> = Concentration of CO<sub>2</sub>, dry basis, percent.

E<sub>SO2</sub> = Emission rate of SO<sub>2</sub>, ng/J (lb/10<sup>6</sup> Btu).

F<sub>C</sub> = Carbon F-factor from Method 19 for the fuel burned, dscm/J (dscf/10<sup>6</sup> Btu).

m<sub>wi</sub> = Initial weight of impingers, bubblers, and moisture absorber, g.

m<sub>wf</sub> = Final weight of impingers, bubblers, and moisture absorber, g.

m<sub>ai</sub> = Initial weight of CO<sub>2</sub> absorber, g.

m<sub>af</sub> = Final weight of CO<sub>2</sub> absorber, g.

m<sub>SO2</sub> = Mass of SO<sub>2</sub> collected, mg.

V<sub>CO2(std)</sub> = Equivalent volume of CO<sub>2</sub> collected at standard conditions, dscm (dscf).

V<sub>w(std)</sub> = Equivalent volume of moisture collected at standard conditions, scm (scf).

12.2 CO<sub>2</sub> Volume Collected, Corrected to Standard Conditions.

$$V_{CO2(std)} = K_3 (m_{af} - m_{ai}) \quad \text{Eq. 6A-1}$$

Where:

K<sub>3</sub> = Equivalent volume of gaseous CO<sub>2</sub> at standard conditions, 5.467 × 10<sup>-4</sup> dscm/g (1.930 × 10<sup>-2</sup> dscf/g).

12.3 Moisture Volume Collected, Corrected to Standard Conditions.

$$V_{w(std)} = K_4 (m_{wf} - m_{wi}) \quad \text{Eq. 6A-2}$$

Where:

K<sub>4</sub> = Equivalent volume of water vapor at standard conditions, 1.336 × 10<sup>-3</sup> scm/g (4.717 × 10<sup>-2</sup> scf/g).

12.4 SO<sub>2</sub> Concentration.

$$C_{SO2} = \frac{K_2 N (V_t - V_{tb}) (V_{soIn} / V_a)}{V_{m(std)} + V_{CO2(std)}} \quad \text{Eq. 6A-3}$$

Where:

K<sub>2</sub> = 32.03 mg SO<sub>2</sub>/meq. SO<sub>2</sub> (7.061 × 10<sup>-5</sup> lb SO<sub>2</sub>/meq. SO<sub>2</sub>)

12.5 CO<sub>2</sub> Concentration.

$$C_{CO2} = \frac{V_{CO2(std)}}{V_{m(std)} + V_{CO2(std)}} \quad \text{Eq. 6A-4}$$

12.6 Moisture Concentration.

$$C_w = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)} + V_{CO2(std)}} \quad \text{Eq. 6A-5}$$

### 13.0 Method Performance

13.1 Range and Precision. The minimum detectable limit and the upper limit for the measurement of SO<sub>2</sub> are the same as for Method 6. For a 20-

liter sample, this method has a precision of ±0.5 percent CO<sub>2</sub> for concentrations between 2.5 and 25 percent CO<sub>2</sub> and ±1.0 percent moisture for moisture concentrations greater than 5 percent.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management. [Reserved]

16.0 Alternative Methods

If the only emission measurement desired is in terms of emission rate of SO<sub>2</sub> (ng/J or lb/10<sup>6</sup> Btu), an abbreviated

procedure may be used. The differences between the above procedure and the abbreviated procedure are described below.

16.1 Sampling Train. The sampling train is the same as that shown in Figure 6A-1 and as described in Section 6.1, except that the dry gas meter is not needed.

16.2 Preparation of the Sampling Train. Follow the same procedure as in

Section 8.1, except do not weigh the isopropanol bubbler, the SO<sub>2</sub> absorbing impingers, or the moisture absorber.

16.3 Sampling Train Leak-Check Procedure and Sample Collection. Leak-check and operate the sampling train as described in Section 8.2, except that dry gas meter readings, barometric pressure, and dry gas meter temperatures need not be recorded during sampling.

16.4 Sample Recovery. Follow the procedure in Section 8.3, except do not weigh the isopropanol bubbler, the SO<sub>2</sub> absorbing impingers, or the moisture absorber.

16.5 Sample Analysis. Analysis of the peroxide solution and QA audit samples is the same as that described in Sections 11.1 and 11.2, respectively.

16.6 Calculations.

16.6.1 SO<sub>2</sub> Collected.

$$m_{\text{SO}_2} = K_2 N (V_t - V_{\text{tb}}) (V_{\text{soln}} / V_a) \quad \text{Eq. 6A-6}$$

Where:

$K_2 = 32.03 \text{ mg SO}_2/\text{meq. SO}_2$

$K_2 = 7.061 \times 10^{-5} \text{ lb SO}_2/\text{meq. SO}_2$

16.6.2 Sulfur Dioxide Emission Rate.

$$E_{\text{SO}_2} = K_5 F_c m_{\text{so}_2} / (m_{\text{af}} - m_{\text{ai}}) \quad \text{Eq. 6A-7}$$

Where:

$K_5 = 1.829 \times 10^9 \text{ mg/dscm}$

$K_2 = 0.1142 \text{ lb/dscf}$

#### 17.0 References

Same as Method 6, Section 17.0, References 1 through 8, with the addition of the following:

1. Stanley, Jon and P.R. Westlin. An Alternate Method for Stack Gas Moisture Determination. Source Evaluation Society Newsletter. 3(4). November 1978.

2. Whittle, Richard N. and P.R. Westlin. Air Pollution Test Report: Development and Evaluation of an Intermittent Integrated SO<sub>2</sub>/CO<sub>2</sub> Emission Sampling Procedure. Environmental Protection Agency, Emission

Standard and Engineering Division, Emission Measurement Branch. Research Triangle Park, NC. December 1979. 14 pp.

**BILLING CODE 6560-50-P**

## 18.0 Tables, Diagrams, Flowcharts, and Validation Data

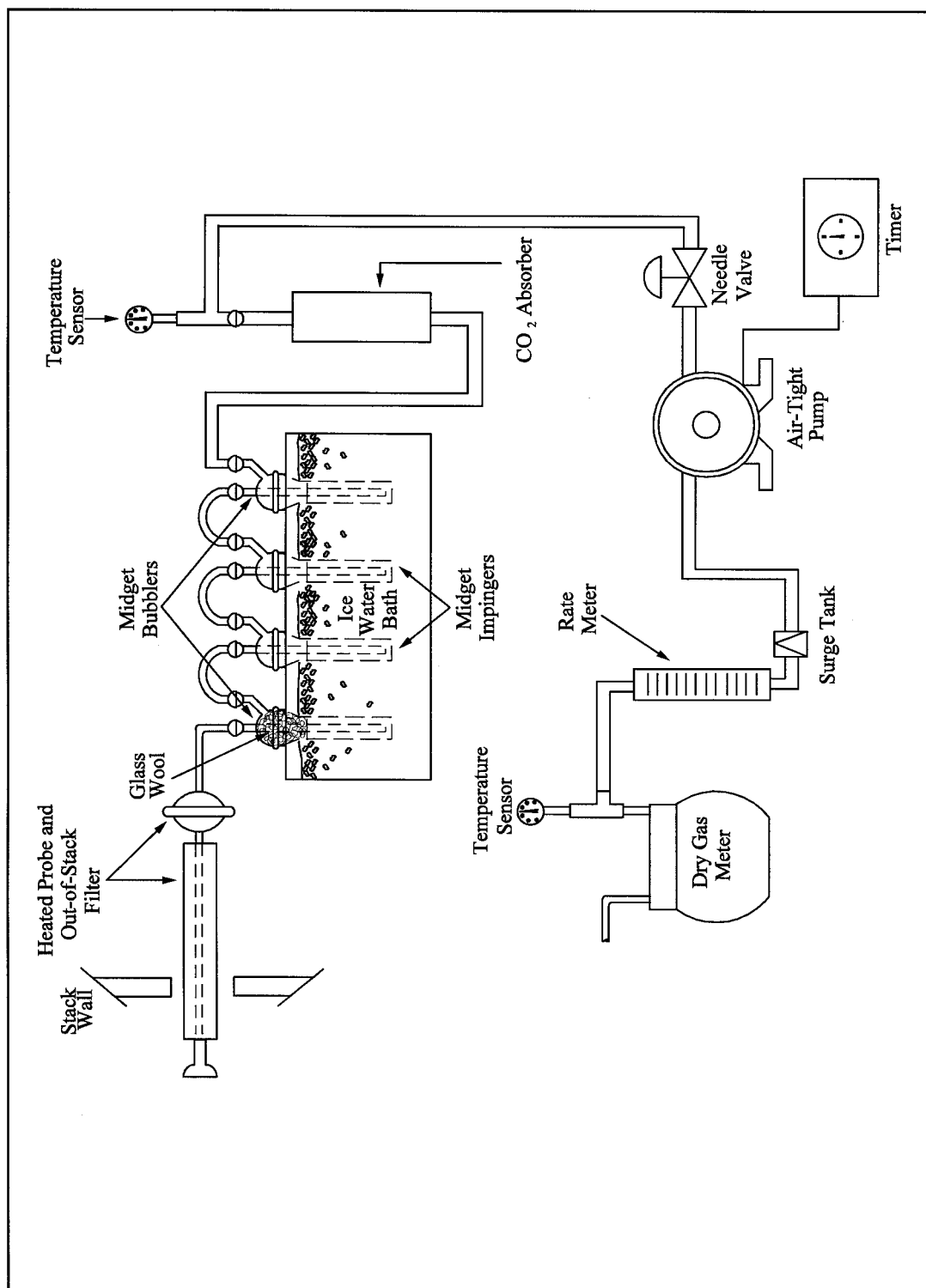


Figure 6A-1. Sampling train.

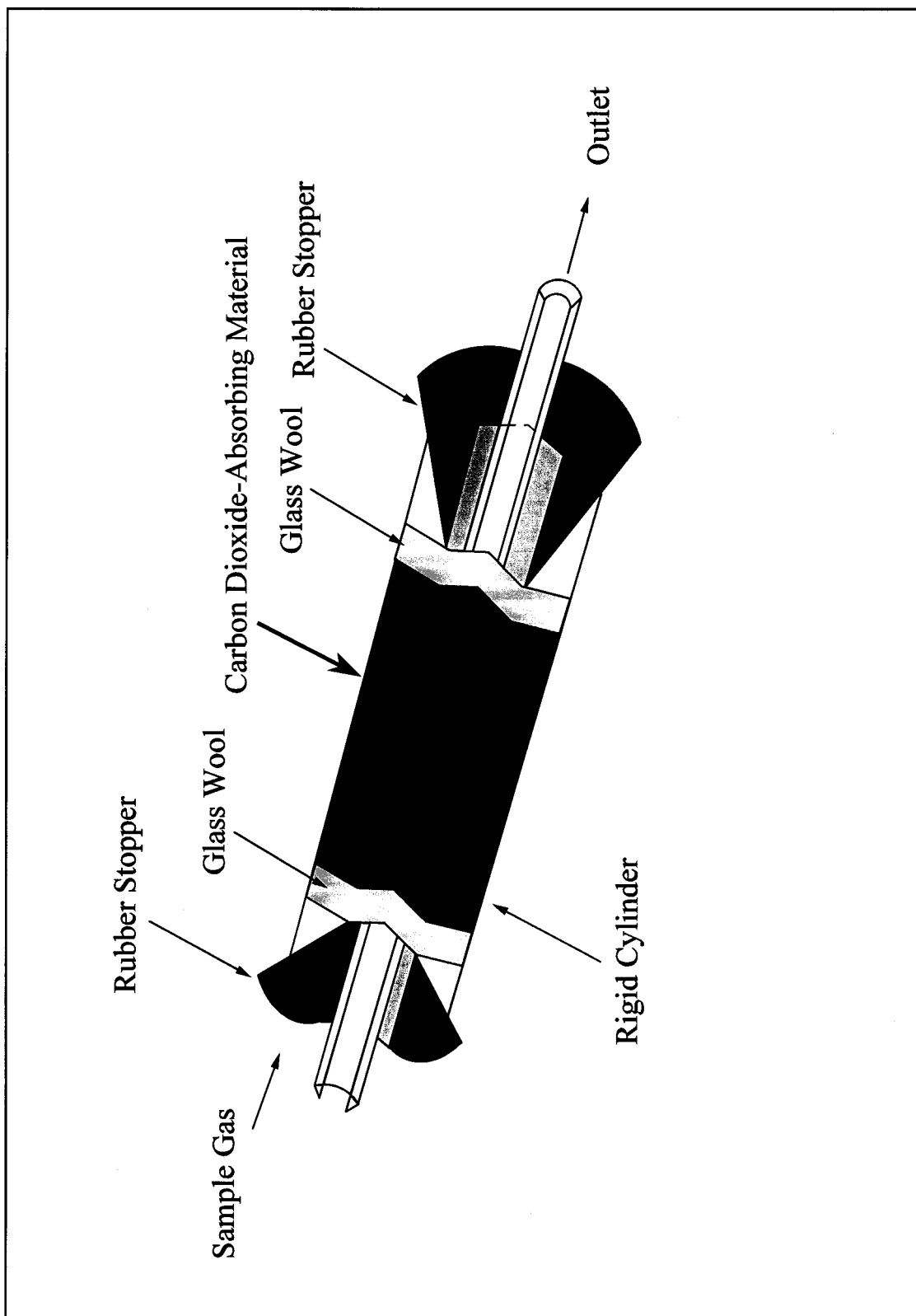


Figure 6A-2. CO<sub>2</sub> Absorber



## Method 6B—Determination of Sulfur Dioxide and Carbon Dioxide Daily Average Emissions From Fossil Fuel Combustion Sources

**Note:** This method does not include all of the specifications (e.g., equipment and

supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test

methods: Method 1, Method 2, Method 3, Method 5, Method 6, and Method 6A.

### 1.0 Scope and Application

#### 1.1 Analytes.

Analyte	CAS No.	Sensitivity
Sulfur dioxide (SO <sub>2</sub> ) .....	7449-09-05	3.4 mg SO <sub>2</sub> /m <sup>3</sup> (2.12 × 10 <sup>-7</sup> lb/ft <sup>3</sup> )
Carbon dioxide (CO <sub>2</sub> ) .....	124-38-9	N/A

1.2 Applicability. This method is applicable for the determination of SO<sub>2</sub> emissions from combustion sources in terms of concentration (ng/dscm or lb/dscf) and emission rate (ng/J or lb/10<sup>6</sup> Btu), and for the determination of CO<sub>2</sub> concentration (percent) on a daily (24 hours) basis.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

### 2.0 Summary of Method

2.1 A gas sample is extracted from the sampling point in the stack intermittently over a 24-hour or other specified time period. The SO<sub>2</sub> fraction is measured by the barium-thorin titration method. Moisture and CO<sub>2</sub> fractions are collected in the same sampling train, and are determined gravimetrically.

### 3.0 Definitions. [Reserved]

### 4.0 Interferences

Same as Method 6, Section 4.0.

### 5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. Same as Method 6, Section 5.2.

### 6.0 Equipment and Supplies

Same as Method 6A, Section 6.0, with the following exceptions and additions:

6.1 The isopropanol bubbler is not used. An empty bubbler for the collection of liquid droplets, that does not allow direct contact between the collected liquid and the gas sample, may be included in the sampling train.

6.2 For intermittent operation, include an industrial timer-switch

designed to operate in the "on" position at least 2 minutes continuously and "off" the remaining period over a repeating cycle. The cycle of operation is designated in the applicable regulation. At a minimum, the sampling operation should include at least 12, equal, evenly-spaced periods per 24 hours.

6.3 Stainless steel sampling probes, type 316, are not recommended for use with Method 6B because of potential sample contamination due to corrosion. Glass probes or other types of stainless steel, e.g., Hasteloy or Carpenter 20, are recommended for long-term use.

**Note:** For applications downstream of wet scrubbers, a heated out-of-stack filter (either borosilicate glass wool or glass fiber mat) is necessary. Probe and filter heating systems capable of maintaining a sample gas temperature of between 20 and 120 °C (68 and 248 °F) at the filter are also required in these cases. The electric supply for these heating systems should be continuous and separate from the timed operation of the sample pump.

### 7.0 Reagents and Standards

Same as Method 6A, Section 7.0, with the following exceptions:

7.1 Isopropanol is not used for sampling.

7.2 The hydrogen peroxide absorbing solution shall be diluted to no less than 6 percent by volume, instead of 3 percent as specified in Methods 6 and 6A.

7.3 If the Method 6B sampling train is to be operated in a low sample flow condition (less than 100 ml/min or 0.21 ft<sup>3</sup>/hr), molecular sieve material may be substituted for Ascarite II as the CO<sub>2</sub> absorbing material. The recommended molecular sieve material is Union Carbide 1/16 inch pellets, 5 Å, or equivalent. Molecular sieve material need not be discarded following the sampling run, provided that it is regenerated as per the manufacturer's instruction. Use of molecular sieve material at flow rates higher than 100 ml/min (0.21 ft<sup>3</sup>/hr) may cause erroneous CO<sub>2</sub> results.

### 8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Preparation of Sampling Train. Same as Method 6A, Section 8.1, with the addition of the following:

8.1.1 The sampling train is assembled as shown in Figure 6A-1 of Method 6A, except that the isopropanol bubbler is not included.

8.1.2 Adjust the timer-switch to operate in the "on" position from 2 to 4 minutes on a 2-hour repeating cycle or other cycle specified in the applicable regulation. Other timer sequences may be used with the restriction that the total sample volume collected is between 25 and 60 liters (0.9 and 2.1 ft<sup>3</sup>) for the amounts of sampling reagents prescribed in this method.

8.1.3 Add cold water to the tank until the impingers and bubblers are covered at least two-thirds of their length. The impingers and bubbler tank must be covered and protected from intense heat and direct sunlight. If freezing conditions exist, the impinger solution and the water bath must be protected.

**Note:** Sampling may be conducted continuously if a low flow-rate sample pump [20 to 40 ml/min (0.04 to 0.08 ft<sup>3</sup>/hr) for the reagent volumes described in this method] is used. If sampling is continuous, the timer-switch is not necessary. In addition, if the sample pump is designed for constant rate sampling, the rate meter may be deleted. The total gas volume collected should be between 25 and 60 liters (0.9 and 2.1 ft<sup>3</sup>) for the amounts of sampling reagents prescribed in this method.

8.2 Sampling Train Leak-Check Procedure. Same as Method 6, Section 8.2.

#### 8.3 Sample Collection.

8.3.1 The probe and filter (either in-stack, out-of-stack, or both) must be heated to a temperature sufficient to prevent water condensation.

8.3.2 Record the initial dry gas meter reading. To begin sampling, position the tip of the probe at the sampling point, connect the probe to the first impinger (or filter), and start the timer and the sample pump. Adjust the sample flow to

a constant rate of approximately 1.0 liter/min (0.035 cfm) as indicated by the rotameter. Observe the operation of the timer, and determine that it is operating as intended (*i.e.*, the timer is in the "on" position for the desired period, and the cycle repeats as required).

8.3.3 One time between 9 a.m. and 11 a.m. during the 24-hour sampling period, record the dry gas meter temperature ( $T_m$ ) and the barometric pressure ( $P_{bar}$ ).

8.3.4 At the conclusion of the run, turn off the timer and the sample pump, remove the probe from the stack, and record the final gas meter volume reading. Conduct a leak-check as described in Section 8.2. If a leak is found, void the test run or use procedures acceptable to the Administrator to adjust the sample volume for leakage. Repeat the steps in Sections 8.3.1 to 8.3.4 for successive runs.

8.4 Sample Recovery. The procedures for sample recovery (moisture measurement, peroxide solution, and CO<sub>2</sub> absorber) are the same as those in Method 6A, Section 8.3.

9.0 Quality Control

Same as Method 6, Section 9.0., with the exception of the isopropanol-check.

10.0 Calibration and Standardization

Same as Method 6, Section 10.0, with the addition of the following:

10.1 Periodic Calibration Check. After 30 days of operation of the test train, conduct a calibration check according to the same procedures as the post-test calibration check (Method 6, Section 10.1.2). If the deviation between initial and periodic calibration factors exceeds 5 percent, use the smaller of the two factors in calculations for the preceding 30 days of data, but use the

most recent calibration factor for succeeding test runs.

11.0 Analytical Procedures

11.1 Sample Loss Check and Analysis. Same as Method 6, Sections 11.1 and 11.2, respectively.

11.2 Quality Assurance (QA) Audit Samples. Analysis of QA audit samples is required only when this method is used for compliance determinations. Obtain an audit sample set as directed in Section 7.3.6 of Method 6. Analyze the audit samples at least once for every 30 days of sample collection, and report the results as directed in Section 11.3 of Method 6. The analyst performing the sample analyses shall perform the audit analyses. If more than one analyst performs the sample analyses during the 30-day sampling period, each analyst shall perform the audit analyses and all audit results shall be reported. Acceptance criteria for the audit results are the same as those in Method 6.

12.0 Data Analysis and Calculations

Same as Method 6A, Section 12.0, except that  $P_{bar}$  and  $T_m$  correspond to the values recorded in Section 8.3.3 of this method. The values are as follows:

$P_{bar}$  = Initial barometric pressure for the test period, mm Hg.

$T_m$  = Absolute meter temperature for the test period, °K.

13.0 Method Performance

13.1 Range.

13.1.1 Sulfur Dioxide. Same as Method 6.

13.1.2 Carbon Dioxide. Not determined.

13.2 Repeatability and Reproducibility. EPA-sponsored collaborative studies were undertaken to determine the magnitude of repeatability and reproducibility

achievable by qualified testers following the procedures in this method. The results of the studies evolve from 145 field tests including comparisons with Methods 3 and 6. For measurements of emission rates from wet, flue gas desulfurization units in (ng/J), the repeatability (intra-laboratory precision) is 8.0 percent and the reproducibility (inter-laboratory precision) is 11.1 percent.

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 Alternative Methods

Same as Method 6A, Section 16.0, except that the timer is needed and is operated as outlined in this method.

17.0 References

Same as Method 6A, Section 17.0, with the addition of the following:

1. Butler, Frank E., et. al. The Collaborative Test of Method 6B: Twenty-Four-Hour Analysis of SO<sub>2</sub> and CO<sub>2</sub>. JAPCA. Vol. 33, No. 10. October 1983.

18.0 Tables, Diagrams, Flowcharts, and Validation Data. [Reserved]

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Method 7—Determination of Nitrogen Oxide Emissions From Stationary Sources

**Note:** This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1 and Method 5.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO <sub>x</sub> ), as NO <sub>2</sub> , including:		
Nitric oxide (NO) .....	10102-43-9	2-400 mg/dscm
Nitrogen dioxide (NO <sub>2</sub> ) .....	10102-44-0	

1.2 Applicability. This method is applicable for the measurement of nitrogen oxides (NO<sub>x</sub>) emitted from stationary sources.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sample methods.

2.0 Summary of Method

A grab sample is collected in an evacuated flask containing a dilute

sulfuric acid-hydrogen peroxide absorbing solution, and the nitrogen oxides, except nitrous oxide, are measured colorimetrically using the phenoldisulfonic acid (PDS) procedure.

3.0 Definitions. [Reserved]

4.0 Interferences

Biased results have been observed when sampling under conditions of high sulfur dioxide concentrations (above 2000 ppm).

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous.

Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide ( $\text{H}_2\text{O}_2$ ).

Irritating to eyes, skin, nose, and lungs.

5.2.2 Phenoldisulfonic Acid.

Irritating to eyes and skin.

5.2.3 Sodium Hydroxide ( $\text{NaOH}$ ).

Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.4 Sulfuric Acid ( $\text{H}_2\text{SO}_4$ ). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/m<sup>3</sup> for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

5.2.5 Phenol. Poisonous and caustic. Do not handle with bare hands as it is absorbed through the skin.

## 6.0 Equipment and Supplies

6.1 Sample Collection. A schematic of the sampling train used in performing this method is shown in Figure 7-1. Other grab sampling systems or equipment, capable of measuring sample volume to within 2.0 percent and collecting a sufficient sample volume to allow analytical reproducibility to within 5 percent, will be considered acceptable alternatives, subject to the approval of the Administrator. The following items are required for sample collection:

6.1.1 Probe. Borosilicate glass tubing, sufficiently heated to prevent water condensation and equipped with an in-stack or heated out-of-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose). Stainless steel or Teflon tubing may also be used for the probe. Heating is not necessary if the probe remains dry during the purging period.

6.1.2 Collection Flask. Two-liter borosilicate, round bottom flask, with short neck and 24/40 standard taper opening, protected against implosion or breakage.

6.1.3 Flask Valve. T-bore stopcock connected to a 24/40 standard taper joint.

6.1.4 Temperature Gauge. Dial-type thermometer, or other temperature gauge, capable of measuring 1 °C (2 °F) intervals from -5 to 50 °C (23 to 122 °F).

6.1.5 Vacuum Line. Tubing capable of withstanding a vacuum of 75 mm (3 in.) Hg absolute pressure, with "T" connection and T-bore stopcock.

6.1.6 Vacuum Gauge. U-tube manometer, 1 meter (39 in.), with 1 mm (0.04 in.) divisions, or other gauge capable of measuring pressure to within 2.5 mm (0.10 in.) Hg.

6.1.7 Pump. Capable of evacuating the collection flask to a pressure equal to or less than 75 mm (3 in.) Hg absolute.

6.1.8 Squeeze Bulb. One-way.

6.1.9 Volumetric Pipette. 25-ml.

6.1.10 Stopcock and Ground Joint Grease. A high-vacuum, high-temperature chlorofluorocarbon grease is required. Halocarbon 25-5S has been found to be effective.

6.1.11 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm (0.1 in.) Hg. See **NOTE** in Method 5, Section 6.1.2.

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Graduated Cylinder. 50-ml with 1 ml divisions.

6.2.2 Storage Containers. Leak-free polyethylene bottles.

6.2.3 Wash Bottle. Polyethylene or glass.

6.2.4 Glass Stirring Rod.

6.2.5 Test Paper for Indicating pH. To cover the pH range of 7 to 14.

6.3 Analysis. The following items are required for analysis:

6.3.1 Volumetric Pipettes. Two 1-ml, two 2-ml, one 3-ml, one 4-ml, two 10-ml, and one 25-ml for each sample and standard.

6.3.2 Porcelain Evaporating Dishes. 175- to 250-ml capacity with lip for pouring, one for each sample and each standard. The Coors No. 45006 (shallowform, 195-ml) has been found to be satisfactory. Alternatively, polymethyl pentene beakers (Nalge No. 1203, 150-ml), or glass beakers (150-ml) may be used. When glass beakers are used, etching of the beakers may cause solid matter to be present in the analytical step; the solids should be removed by filtration.

6.3.3 Steam Bath. Low-temperature ovens or thermostatically controlled hot plates kept below 70 °C (160 °F) are acceptable alternatives.

6.3.4 Dropping Pipette or Dropper. Three required.

6.3.5 Polyethylene Policeman. One for each sample and each standard.

6.3.6 Graduated Cylinder. 100-ml with 1-ml divisions.

6.3.7 Volumetric Flasks. 50-ml (one for each sample and each standard), 100-ml (one for each sample and each standard, and one for the working

standard  $\text{KNO}_3$  solution), and 1000-ml (one).

6.3.8 Spectrophotometer. To measure at 410 nm.

6.3.9 Graduated Pipette. 10-ml with 0.1-ml divisions.

6.3.10 Test Paper for Indicating pH. To cover the pH range of 7 to 14.

6.3.11 Analytical Balance. To measure to within 0.1 mg.

## 7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection. The following reagents are required for sampling:

7.1.1 Water. Deionized distilled to conform to ASTM D 1193-77 or 91 Type 3 (incorporated by reference—see § 60.17). The  $\text{KMnO}_4$  test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.1.2 Absorbing Solution. Cautiously add 2.8 ml concentrated  $\text{H}_2\text{SO}_4$  to a 1-liter flask partially filled with water. Mix well, and add 6 ml of 3 percent hydrogen peroxide, freshly prepared from 30 percent hydrogen peroxide solution. Dilute to 1 liter of water and mix well. The absorbing solution should be used within 1 week of its preparation. Do not expose to extreme heat or direct sunlight.

7.2 Sample Recovery. The following reagents are required for sample recovery:

7.2.1 Water. Same as in 7.1.1.

7.2.2 Sodium Hydroxide, 1 N.

Dissolve 40 g  $\text{NaOH}$  in water, and dilute to 1 liter.

7.3 Analysis. The following reagents and standards are required for analysis:

7.3.1 Water. Same as in 7.1.1.

7.3.2 Fuming Sulfuric Acid. 15 to 18 percent by weight free sulfur trioxide. **HANDLE WITH CAUTION.**

7.3.3 Phenol. White solid.

7.3.4 Sulfuric Acid. Concentrated, 95 percent minimum assay.

7.3.5 Potassium Nitrate ( $\text{KNO}_3$ ). Dried at 105 to 110 °C (221 to 230 °F) for a minimum of 2 hours just prior to preparation of standard solution.

7.3.6 Standard  $\text{KNO}_3$  Solution. Dissolve exactly 2.198 g of dried  $\text{KNO}_3$  in water, and dilute to 1 liter with water in a 1000-ml volumetric flask.

7.3.7 Working Standard  $\text{KNO}_3$  Solution. Dilute 10 ml of the standard solution to 100 ml with water. One ml of the working standard solution is equivalent to 100 µg nitrogen dioxide ( $\text{NO}_2$ ).

7.3.8 Phenoldisulfonic Acid Solution. Dissolve 25 g of pure white phenol solid in 150 ml concentrated sulfuric acid on a steam bath. Cool, add 75 ml fuming sulfuric acid (15 to 18 percent by weight free sulfur trioxide—HANDLE WITH CAUTION), and heat at 100 °C (212 °F) for 2 hours. Store in a dark, stoppered bottle.

7.3.9 Concentrated Ammonium Hydroxide.

7.3.10 Quality Assurance Audit Samples. When making compliance determinations, and upon availability, audit samples may be obtained from the appropriate EPA Regional Office or from the responsible enforcement authority.

**Note:** The responsible enforcement authority should be notified at least 30 days prior to the test date to allow sufficient time for sample delivery.

8.0 Sample Collection, Preservation, Storage and Transport

8.1 Sample Collection.

8.1.1 Flask Volume. The volume of the collection flask and flask valve combination must be known prior to sampling. Assemble the flask and flask valve, and fill with water to the stopcock. Measure the volume of water to ±10 ml. Record this volume on the flask.

8.1.2 Pipette 25 ml of absorbing solution into a sample flask, retaining a sufficient quantity for use in preparing the calibration standards. Insert the flask valve stopper into the flask with the valve in the “purge” position. Assemble the sampling train as shown in Figure 7–1, and place the probe at the sampling point. Make sure that all fittings are tight and leak-free, and that all ground glass joints have been greased properly with a high-vacuum, high temperature chlorofluorocarbon-based stopcock grease. Turn the flask valve and the pump valve to their “evacuate” positions. Evacuate the flask to 75 mm

(3 in.) Hg absolute pressure, or less. Evacuation to a pressure approaching the vapor pressure of water at the existing temperature is desirable. Turn the pump valve to its “vent” position, and turn off the pump. Check for leakage by observing the manometer for any pressure fluctuation. (Any variation greater than 10 mm (0.4 in.) Hg over a period of 1 minute is not acceptable, and the flask is not to be used until the leakage problem is corrected. Pressure in the flask is not to exceed 75 mm (3 in.) Hg absolute at the time sampling is commenced.) Record the volume of the flask and valve ( $V_f$ ), the flask temperature ( $T_f$ ), and the barometric pressure. Turn the flask valve counterclockwise to its “purge” position, and do the same with the pump valve. Purge the probe and the vacuum tube using the squeeze bulb. If condensation occurs in the probe and the flask valve area, heat the probe, and purge until the condensation disappears. Next, turn the pump valve to its “vent” position. Turn the flask valve clockwise to its “evacuate” position, and record the difference in the mercury levels in the manometer. The absolute internal pressure in the flask ( $P_i$ ) is equal to the barometric pressure less the manometer reading. Immediately turn the flask valve to the “sample” position, and permit the gas to enter the flask until pressures in the flask and sample line (*i.e.*, duct, stack) are equal. This will usually require about 15 seconds; a longer period indicates a plug in the probe, which must be corrected before sampling is continued. After collecting the sample, turn the flask valve to its “purge” position, and disconnect the flask from the sampling train.

8.1.3 Shake the flask for at least 5 minutes.

8.1.4 If the gas being sampled contains insufficient oxygen for the

conversion of NO to NO<sub>2</sub> (*e.g.*, an applicable subpart of the standards may require taking a sample of a calibration gas mixture of NO in N<sub>2</sub>), then introduce oxygen into the flask to permit this conversion. Oxygen may be introduced into the flask by one of three methods: (1) Before evacuating the sampling flask, flush with pure cylinder oxygen, then evacuate flask to 75 mm (3 in.) Hg absolute pressure or less; or (2) inject oxygen into the flask after sampling; or (3) terminate sampling with a minimum of 50 mm (2 in.) Hg vacuum remaining in the flask, record this final pressure, and then vent the flask to the atmosphere until the flask pressure is almost equal to atmospheric pressure.

8.2 Sample Recovery. Let the flask sit for a minimum of 16 hours, and then shake the contents for 2 minutes.

8.2.1 Connect the flask to a mercury filled U-tube manometer. Open the valve from the flask to the manometer, and record the flask temperature ( $T_f$ ), the barometric pressure, and the difference between the mercury levels in the manometer. The absolute internal pressure in the flask ( $P_i$ ) is the barometric pressure less the manometer reading. Transfer the contents of the flask to a leak-free polyethylene bottle. Rinse the flask twice with 5 ml portions of water, and add the rinse water to the bottle. Adjust the pH to between 9 and 12 by adding 1 N NaOH, dropwise (about 25 to 35 drops). Check the pH by dipping a stirring rod into the solution and then touching the rod to the pH test paper. Remove as little material as possible during this step. Mark the height of the liquid level so that the container can be checked for leakage after transport. Label the container to identify clearly its contents. Seal the container for shipping.

9.0 Quality Control

Section	Quality control measure	Effect
10.1 .....	Spectrophotometer calibration .....	Ensure linearity of spectrophotometer response to standards.
11.4 .....	Audit sample analysis .....	Evaluate analytical technique, preparation of standards.

10.0 Calibration and Standardization

10.1 Spectrophotometer.

10.1.1 Optimum Wavelength Determination.

10.1.1.1 Calibrate the wavelength scale of the spectrophotometer every 6 months. The calibration may be accomplished by using an energy source with an intense line emission such as a mercury lamp, or by using a series of glass filters spanning the measuring range of the spectrophotometer.

Calibration materials are available commercially and from the National Institute of Standards and Technology. Specific details on the use of such materials should be supplied by the vendor; general information about calibration techniques can be obtained from general reference books on analytical chemistry. The wavelength scale of the spectrophotometer must read correctly within 5 nm at all calibration points; otherwise, repair and

recalibrate the spectrophotometer. Once the wavelength scale of the spectrophotometer is in proper calibration, use 410 nm as the optimum wavelength for the measurement of the absorbance of the standards and samples.

10.1.1.2 Alternatively, a scanning procedure may be employed to determine the proper measuring wavelength. If the instrument is a double-beam spectrophotometer, scan the spectrum between 400 and 415 nm

using a 200  $\mu\text{g}$   $\text{NO}_2$  standard solution in the sample cell and a blank solution in the reference cell. If a peak does not occur, the spectrophotometer is probably malfunctioning and should be repaired. When a peak is obtained within the 400 to 415 nm range, the wavelength at which this peak occurs shall be the optimum wavelength for the measurement of absorbance of both the standards and the samples. For a single-beam spectrophotometer, follow the scanning procedure described above, except scan separately the blank and standard solutions. The optimum wavelength shall be the wavelength at which the maximum difference in absorbance between the standard and the blank occurs.

**10.1.2 Determination of Spectrophotometer Calibration Factor  $K_c$ .** Add 0 ml, 2.0 ml, 4.0 ml, 6.0 ml, and 8.0 ml of the  $\text{KNO}_3$  working standard solution (1 ml = 100  $\mu\text{g}$   $\text{NO}_2$ ) to a series of five 50-ml volumetric flasks. To each flask, add 25 ml of absorbing solution and 10 ml water. Add 1 N NaOH to each flask until the pH is between 9 and 12 (about 25 to 35 drops). Dilute to the mark with water. Mix thoroughly, and pipette a 25-ml aliquot of each solution into a separate porcelain evaporating dish. Beginning with the evaporation step, follow the analysis procedure of Section 11.2 until the solution has been transferred to the 100-ml volumetric flask and diluted to the mark. Measure the absorbance of each solution at the optimum wavelength as determined in Section 10.2.1. This calibration procedure must be repeated on each day that samples are analyzed. Calculate the spectrophotometer calibration factor as shown in Section 12.2.

**10.1.3 Spectrophotometer Calibration Quality Control.** Multiply the absorbance value obtained for each standard by the  $K_c$  factor (reciprocal of the least squares slope) to determine the distance each calibration point lies from the theoretical calibration line. The difference between the calculated concentration values and the actual concentrations (*i.e.*, 100, 200, 300, and 400  $\mu\text{g}$   $\text{NO}_2$ ) should be less than 7 percent for all standards.

**10.2 Barometer.** Calibrate against a mercury barometer.

**10.3 Temperature Gauge.** Calibrate dial thermometers against mercury-in-glass thermometers.

**10.4 Vacuum Gauge.** Calibrate mechanical gauges, if used, against a mercury manometer such as that specified in Section 6.1.6.

**10.5 Analytical Balance.** Calibrate against standard weights.

## 11.0 Analytical Procedures

**11.1 Sample Loss Check.** Note the level of the liquid in the container, and confirm whether any sample was lost during shipment. Note this on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

**11.2 Sample Preparation.** Immediately prior to analysis, transfer the contents of the shipping container to a 50 ml volumetric flask, and rinse the container twice with 5 ml portions of water. Add the rinse water to the flask, and dilute to mark with water; mix thoroughly. Pipette a 25-ml aliquot into the porcelain evaporating dish. Return any unused portion of the sample to the polyethylene storage bottle. Evaporate the 25-ml aliquot to dryness on a steam bath, and allow to cool. Add 2 ml phenoldisulfonic acid solution to the dried residue, and triturate thoroughly with a polyethylene policeman. Make sure the solution contacts all the residue. Add 1 ml water and 4 drops of concentrated sulfuric acid. Heat the solution on a steam bath for 3 minutes with occasional stirring. Allow the solution to cool, add 20 ml water, mix well by stirring, and add concentrated ammonium hydroxide, dropwise, with constant stirring, until the pH is 10 (as determined by pH paper). If the sample contains solids, these must be removed by filtration (centrifugation is an acceptable alternative, subject to the approval of the Administrator) as follows: Filter through Whatman No. 41 filter paper into a 100-ml volumetric flask. Rinse the evaporating dish with three 5-ml portions of water. Filter these three rinses. Wash the filter with at least three 15-ml portions of water. Add the filter washings to the contents of the volumetric flask, and dilute to the mark with water. If solids are absent, the solution can be transferred directly to the 100-ml volumetric flask and diluted to the mark with water.

**11.3 Sample Analysis.** Mix the contents of the flask thoroughly, and measure the absorbance at the optimum wavelength used for the standards (Section 10.2.1), using the blank solution as a zero reference. Dilute the sample and the blank with equal volumes of water if the absorbance exceeds  $A_4$ , the absorbance of the 400- $\mu\text{g}$   $\text{NO}_2$  standard (see Section 10.2.2).

### 11.4 Audit Sample Analysis.

**11.4.1** When the method is used to analyze samples to demonstrate compliance with a source emission regulation, an audit sample must be analyzed, subject to availability.

**11.4.2** Concurrently analyze the audit sample and the compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation.

**11.4.3** The same analyst, analytical reagents, and analytical system must be used for the compliance samples and the audit sample. If this condition is met, duplicate auditing of subsequent compliance analyses for the same enforcement agency within a 30-day period is waived. An audit sample set may not be used to validate different sets of compliance samples under the jurisdiction of separate enforcement agencies, unless prior arrangements have been made with both enforcement agencies.

### 11.5 Audit Sample Results.

**11.5.1** Calculate the audit sample concentrations and submit results using the instructions provided with the audit samples.

**11.5.2** Report the results of the audit samples and the compliance determination samples along with their identification numbers, and the analyst's name to the responsible enforcement authority. Include this information with reports of any subsequent compliance analyses for the same enforcement authority during the 30-day period.

**11.5.3** The concentrations of the audit samples obtained by the analyst must agree within 5 percent of the actual concentration. If the 5 percent specification is not met, reanalyze the compliance and audit samples, and include initial and reanalysis values in the test report.

**11.5.4** Failure to meet the 5-percent specification may require retests until the audit problems are resolved. However, if the audit results do not affect the compliance or noncompliance status of the affected facility, the Administrator may waive the reanalysis requirement, further audits, or retests and accept the results of the compliance test. While steps are being taken to resolve audit analysis problems, the Administrator may also choose to use the data to determine the compliance or noncompliance status of the affected facility.

## 12.0 Data Analysis and Calculations

Carry out the calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculations.

### 12.1 Nomenclature.

$A$  = Absorbance of sample.

$A_1$  = Absorbance of the 100- $\mu\text{g}$   $\text{NO}_2$  standard.

$A_2$  = Absorbance of the 200- $\mu\text{g}$   $\text{NO}_2$  standard.

A<sub>3</sub> = Absorbance of the 300-μg NO<sub>2</sub> standard.

A<sub>4</sub> = Absorbance of the 400-μg NO<sub>2</sub> standard.

C = Concentration of NO<sub>x</sub> as NO<sub>2</sub>, dry basis, corrected to standard conditions, mg/dsm<sup>3</sup> (lb/dscf).

C<sub>d</sub> = Determined audit sample concentration, mg/dscm.

C<sub>a</sub> = Actual audit sample concentration, mg/dscm.

F = Dilution factor (*i.e.*, 25/5, 25/10, etc., required only if sample dilution was needed to reduce the

absorbance into the range of the calibration).

K<sub>c</sub> = Spectrophotometer calibration factor.

m = Mass of NO<sub>x</sub> as NO<sub>2</sub> in gas sample, μg.

P<sub>f</sub> = Final absolute pressure of flask, mm Hg (in. Hg).

P<sub>i</sub> = Initial absolute pressure of flask, mm Hg (in. Hg).

P<sub>std</sub> = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

RE = Relative error for QA audit samples, percent.

T<sub>f</sub> = Final absolute temperature of flask, °K (°R).

T<sub>i</sub> = Initial absolute temperature of flask, °K (°R).

T<sub>std</sub> = Standard absolute temperature, 293 °K (528 °R).

V<sub>sc</sub> = Sample volume at standard conditions (dry basis), ml.

V<sub>f</sub> = Volume of flask and valve, ml.

V<sub>a</sub> = Volume of absorbing solution, 25 ml.

12.2 Spectrophotometer Calibration Factor.

$$K_c = 100 \frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^2 + A_2^2 + A_3^2 + A_4^2} \quad \text{Eq. 7-1}$$

### 12.3 Sample Volume, Dry Basis, Corrected to Standard Conditions.

$$V_{sc} = (V_f - V_a) \frac{T_{std}}{P_{std}} \left[ \frac{P_f}{T_f} - \frac{P_i}{T_i} \right] \quad \text{Eq. 7-2}$$

$$= K_1 (V_f - 25) \left[ \frac{P_f}{T_f} - \frac{P_i}{T_i} \right]$$

Where:

K<sub>1</sub> = 0.3858 °K/mm Hg for metric units,

K<sub>1</sub> = 17.65 °R/in. Hg for English units.

#### 12.4 Total μg NO<sub>2</sub> per sample.

$$m = 2K_c AF \quad \text{Eq. 7-3}$$

Where:

2 = 50/25, the aliquot factor.

**Note:** If other than a 25-ml aliquot is used for analysis, the factor 2 must be replaced by a corresponding factor.

#### 12.5 Sample Concentration, Dry Basis, Corrected to Standard Conditions.

$$C = K_2 (m/V_{sc}) \quad \text{Eq. 7-4}$$

Where:

K<sub>2</sub> = 10<sup>3</sup> (mg/m<sup>3</sup>)/(μg/ml) for metric units,

K<sub>2</sub> = 6.242 × 10<sup>-5</sup> (lb/scf)/(μg/ml) for English units.

#### 12.6 Relative Error for QA Audit Samples.

$$RE = 100 (C_d - C_a) / C_a \quad \text{Eq. 7-5}$$

### 13.0 Method Performance

13.1 Range. The analytical range of the method has been determined to be 2 to 400 milligrams NO<sub>x</sub> (as NO<sub>2</sub>) per dry standard cubic meter, without having to dilute the sample.

#### 14.0 Pollution Prevention. [Reserved]

#### 15.0 Waste Management. [Reserved]

#### 16.0 References

1. Standard Methods of Chemical Analysis. 6th ed. New York, D. Van Nostrand Co., Inc. 1962. Vol. 1, pp. 329–330.

2. Standard Method of Test for Oxides of Nitrogen in Gaseous Combustion Products (Phenoldisulfonic Acid Procedure). In: 1968 Book of ASTM Standards, Part 26. Philadelphia, PA. 1968. ASTM Designation D 1608–60, pp. 725–729.

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4. Beatty, R.L., L.B. Berger, and H.H. Schrenk. Determination of Oxides of Nitrogen by the Phenoldisulfonic Acid Method. Bureau of Mines, U.S. Dept. of Interior. R.I. 3687. February 1943.

5. Hamil, H.F. and D.E. Camann. Collaborative Study of Method for the Determination of Nitrogen Oxide Emissions from Stationary Sources (Fossil Fuel-Fired Steam Generators). Southwest Research Institute Report for Environmental Protection Agency. Research Triangle Park, NC. October 5, 1973.

6. Hamil, H.F. and R.E. Thomas. Collaborative Study of Method for the Determination of Nitrogen Oxide Emissions from Stationary Sources (Nitric Acid Plants). Southwest Research Institute Report for Environmental Protection Agency. Research Triangle Park, NC. May 8, 1974.

7. Stack Sampling Safety Manual (Draft). U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC. September 1978.

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## 17.0 Tables, Diagrams, Flowcharts, and Validation Data

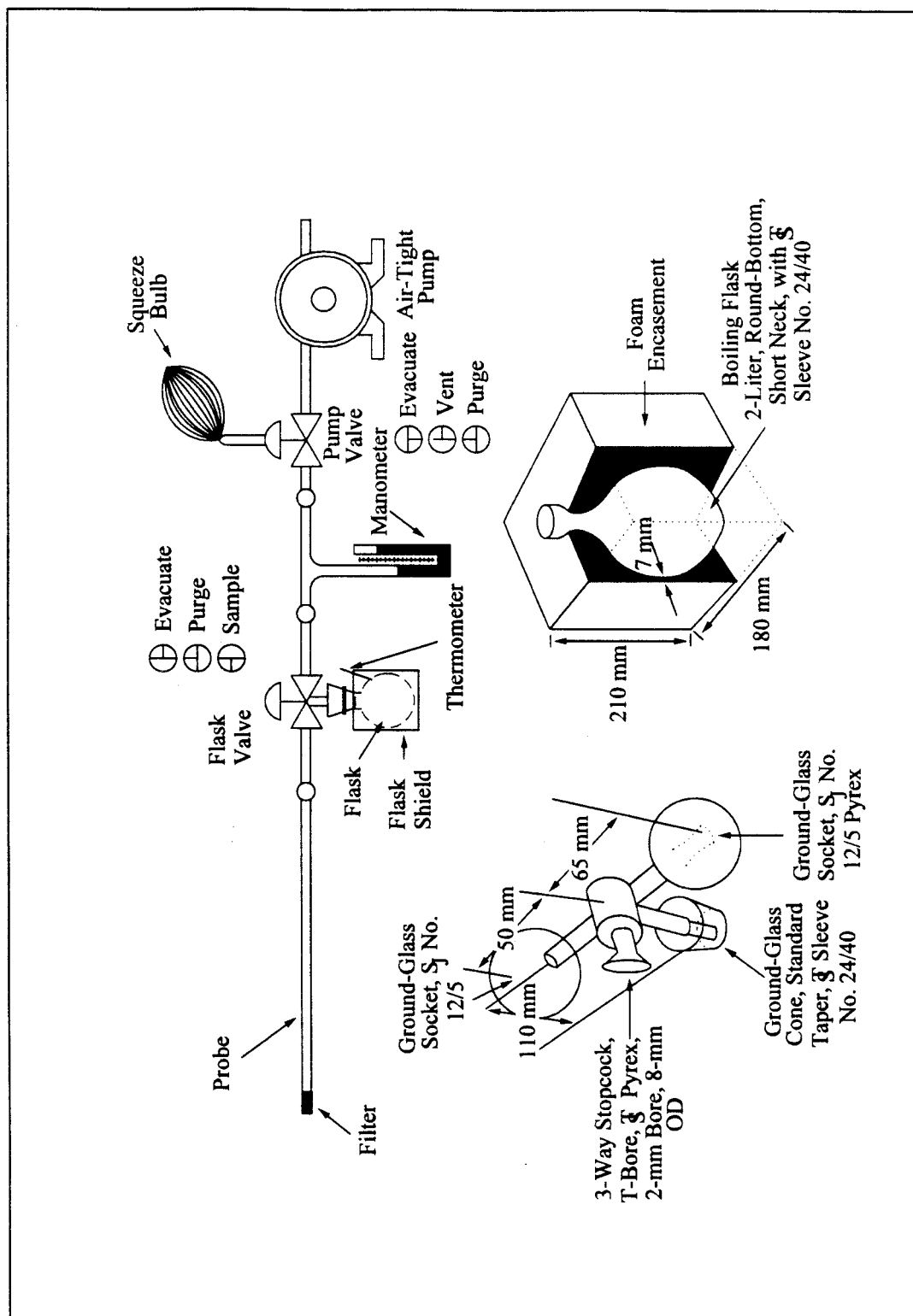


Figure 7-1. Sampling Train, Flask Valve, and Flask.

**Method 7A—Determination of Nitrogen Oxide Emissions From Stationary Sources (Ion Chromatographic Method)**

**Note:** This method does not include all of the specifications (e.g., equipment and

supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge

of at least the following additional test methods: Method 1, Method 3, Method 5, and Method 7.

**1.0 Scope and Application****1.1 Analytes.**

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO <sub>x</sub> ), as NO <sub>2</sub> , including: Nitric oxide (NO) ..... Nitrogen dioxide (NO <sub>2</sub> ) .....	10102-43-9 10102-44-0	65-655 ppmv

1.2 Applicability. This method is applicable for the determination of NO<sub>x</sub> emissions from stationary sources.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

**2.0 Summary of Method**

A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution. The nitrogen oxides, excluding nitrous oxide (N<sub>2</sub>O), are oxidized to nitrate and measured by ion chromatography.

**3.0 Definitions [Reserved]****4.0 Interferences**

Biased results have been observed when sampling under conditions of high sulfur dioxide concentrations (above 2000 ppm).

**5.0 Safety**

5.1 This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>). Irritating to eyes, skin, nose, and lungs.

5.2.2 Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung

tissue damage with edema. 3 mg/m<sup>3</sup> will cause lung damage in uninitiated. 1 mg/m<sup>3</sup> for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

**6.0 Equipment and Supplies**

6.1 Sample Collection. Same as in Method 7, Section 6.1.

6.2 Sample Recovery. Same as in Method 7, Section 6.2, except the stirring rod and pH paper are not needed.

6.3 Analysis. For the analysis, the following equipment and supplies are required. Alternative instrumentation and procedures will be allowed provided the calibration precision requirement in Section 10.1.2 and audit accuracy requirement in Section 11.3 can be met.

6.3.1 Volumetric Pipets. Class A; 1-, 2-, 4-, 5-ml (two for the set of standards and one per sample), 6-, 10-, and graduated 5-ml sizes.

6.3.2 Volumetric Flasks. 50-ml (two per sample and one per standard), 200-ml, and 1-liter sizes.

6.3.3 Analytical Balance. To measure to within 0.1 mg.

6.3.4 Ion Chromatograph. The ion chromatograph should have at least the following components:

6.3.4.1 Columns. An anion separation or other column capable of resolving the nitrate ion from sulfate and other species present and a standard anion suppressor column (optional). Suppressor columns are produced as proprietary items; however, one can be produced in the laboratory using the resin available from BioRad Company, 32nd and Griffin Streets, Richmond, California. Peak resolution can be optimized by varying the eluent strength or column flow rate, or by experimenting with alternative columns that may offer more efficient separation. When using guard columns with the stronger reagent to protect the separation column, the analyst should allow rest periods between injection

intervals to purge possible sulfate buildup in the guard column.

6.3.4.2 Pump. Capable of maintaining a steady flow as required by the system.

6.3.4.3 Flow Gauges. Capable of measuring the specified system flow rate.

6.3.4.4 Conductivity Detector.

6.3.4.5 Recorder. Compatible with the output voltage range of the detector.

**7.0 Reagents and Standards**

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection. Same as Method 7, Section 7.1.

7.2 Sample Recovery. Same as Method 7, Section 7.1.1.

7.3 Analysis. The following reagents and standards are required for analysis:

7.3.1 Water. Same as Method 7, Section 7.1.1.

7.3.2 Stock Standard Solution, 1 mg NO<sub>2</sub>/ml. Dry an adequate amount of sodium nitrate (NaNO<sub>3</sub>) at 105 to 110 °C (221 to 230 °F) for a minimum of 2 hours just before preparing the standard solution. Then dissolve exactly 1.847 g of dried NaNO<sub>3</sub> in water, and dilute to 1 liter in a volumetric flask. Mix well. This solution is stable for 1 month and should not be used beyond this time.

7.3.3 Working Standard Solution, 25 µg/ml. Dilute 5 ml of the standard solution to 200 ml with water in a volumetric flask, and mix well.

7.3.4 Eluent Solution. Weigh 1.018 g of sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) and 1.008 g of sodium bicarbonate (NaHCO<sub>3</sub>), and dissolve in 4 liters of water. This solution is 0.0024 M Na<sub>2</sub>CO<sub>3</sub>/0.003 M NaHCO<sub>3</sub>. Other eluents appropriate to the column type and capable of resolving nitrate ion from sulfate and other species present may be used.

7.3.5 Quality Assurance Audit Samples. Same as Method 7, Section 7.3.8.



**8.0 Sample Collection, Preservation, Storage, and Transport**

8.1 Sampling. Same as in Method 7, Section 8.1.

8.2 Sample Recovery. Same as in Method 7, Section 8.2, except delete the steps on adjusting and checking the pH of the sample. Do not store the samples

more than 4 days between collection and analysis.

**9.0 Quality Control**

Section	Quality control measure	Effect
10.1 .....	Ion chromatograph calibration .....	Ensure linearity of ion chromatograph response to standards.
11.3 .....	Audit sample analysis .....	Evaluate analytical technique, preparation of standards.

**10.0 Calibration and Standardizations****10.1 Ion Chromatograph.**

10.1.1 Determination of Ion Chromatograph Calibration Factor S. Prepare a series of five standards by adding 1.0, 2.0, 4.0, 6.0, and 10.0 ml of working standard solution (25 µg/ml) to a series of five 50-ml volumetric flasks. (The standard masses will equal 25, 50, 100, 150, and 250 µg.) Dilute each flask to the mark with water, and mix well. Analyze with the samples as described in Section 11.2, and subtract the blank from each value. Prepare or calculate a linear regression plot of the standard masses in µg (x-axis) versus their peak height responses in millimeters (y-axis). (Take peak height measurements with symmetrical peaks; in all other cases, calculate peak areas.) From this curve, or equation, determine the slope, and calculate its reciprocal to denote as the calibration factor, S.

10.1.2 Ion Chromatograph Calibration Quality Control. If any point on the calibration curve deviates from the line by more than 7 percent of the concentration at that point, remake and reanalyze that standard. This deviation can be determined by multiplying S times the peak height response for each standard. The resultant concentrations must not differ by more than 7 percent from each known standard mass (*i.e.*, 25, 50, 100, 150, and 250 µg).

10.2 Conductivity Detector. Calibrate according to manufacturer's specifications prior to initial use.

10.3 Barometer. Calibrate against a mercury barometer.

10.4 Temperature Gauge. Calibrate dial thermometers against mercury-in-glass thermometers.

10.5 Vacuum Gauge. Calibrate mechanical gauges, if used, against a mercury manometer such as that specified in Section 6.1.6 of Method 7.

10.6 Analytical Balance. Calibrate against standard weights.

**11.0 Analytical Procedures****11.1 Sample Preparation.**

11.1.1 Note on the analytical data sheet, the level of the liquid in the container, and whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, either

void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Immediately before analysis, transfer the contents of the shipping container to a 50-ml volumetric flask, and rinse the container twice with 5 ml portions of water. Add the rinse water to the flask, and dilute to the mark with water. Mix thoroughly.

11.1.2 Pipet a 5-ml aliquot of the sample into a 50-ml volumetric flask, and dilute to the mark with water. Mix thoroughly. For each set of determinations, prepare a reagent blank by diluting 5 ml of absorbing solution to 50 ml with water. (Alternatively, eluent solution may be used instead of water in all sample, standard, and blank dilutions.)

**11.2 Analysis.**

11.2.1 Prepare a standard calibration curve according to Section 10.1.1. Analyze the set of standards followed by the set of samples using the same injection volume for both standards and samples. Repeat this analysis sequence followed by a final analysis of the standard set. Average the results. The two sample values must agree within 5 percent of their mean for the analysis to be valid. Perform this duplicate analysis sequence on the same day. Dilute any sample and the blank with equal volumes of water if the concentration exceeds that of the highest standard.

11.2.2 Document each sample chromatogram by listing the following analytical parameters: injection point, injection volume, nitrate and sulfate retention times, flow rate, detector sensitivity setting, and recorder chart speed.

11.3 Audit Sample Analysis. Same as Method 7, Section 11.4.

**12.0 Data Analysis and Calculations**

Carry out the calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculations.

12.1 Sample Volume. Calculate the sample volume  $V_{sc}$  (in ml), on a dry basis, corrected to standard conditions, using Equation 7-2 of Method 7.

12.2 Sample Concentration of  $NO_x$  as  $NO_2$ .

12.2.1 Calculate the sample concentration C (in mg/dscm) as follows:

$$C = (H)(S)(F)(10^4)/V_{sc} \quad \text{Eq. 7A-1}$$

Where:

H = Sample peak height, mm.

S = Calibration factor, µg/mm.

F = Dilution factor (required only if sample dilution was needed to reduce the concentration into the range of calibration), dimensionless.

$10^4 = 1:10$  dilution times conversion factor of: (mg/ $10^3$  µg)( $10^6$  ml/ $m^3$ ).

12.2.2 If desired, the concentration of  $NO_2$  may be calculated as ppm  $NO_2$  at standard conditions as follows:

$$\text{ppm } NO_2 = 0.5228C \quad \text{Eq. 7A-2}$$

Where:

0.5228 = ml/mg  $NO_2$ .

**13.0 Method Performance**

13.1 Range. The analytical range of the method is from 125 to 1250 mg  $NO_x/m^3$  as  $NO_2$  (65 to 655 ppmv), and higher concentrations may be analyzed by diluting the sample. The lower detection limit is approximately 19 mg/ $m^3$  (10 ppmv), but may vary among instruments.

**14.0 Pollution Prevention.** [Reserved]

**15.0 Waste Management.** [Reserved]

**16.0 References**

- Mulik, J.D., and E. Sawicki. Ion Chromatographic Analysis of Environmental Pollutants. Ann Arbor, Ann Arbor Science Publishers, Inc. Vol. 2, 1979.
- Sawicki, E., J.D. Mulik, and E. Wittgenstein. Ion Chromatographic Analysis of Environmental Pollutants. Ann Arbor, Ann Arbor Science Publishers, Inc. Vol. 1, 1978.
- Siemer, D.D. Separation of Chloride and Bromide from Complex Matrices Prior to Ion Chromatographic Determination. Anal. Chem. 52(12):1874-1877. October 1980.
- Small, H., T.S. Stevens, and W.C. Bauman. Novel Ion Exchange Chromatographic Method Using Conductimetric Determination. Anal. Chem. 47(11):1801. 1975.

5. Yu, K.K., and P.R. Westlin. Evaluation of Reference Method 7 Flask Reaction Time. Source Evaluation Society Newsletter. 4(4). November 1979. 10 pp.

6. Stack Sampling Safety Manual (Draft). U.S. Environmental Protection Agency, Office of Air Quality Planning and Standard, Research Triangle Park, NC. September 1978.

### 17.0 Tables, Diagrams, Flowcharts, and Validation Data. [Reserved]

#### Method 7B—Determination of Nitrogen Oxide Emissions From Stationary Sources (Ultraviolet Spectrophotometric Method)

**Note:** This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and

analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 5, and Method 7.

### 1.0 Scope and Application

#### 1.1 Analytes.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO <sub>x</sub> ), as NO <sub>2</sub> , including:		
Nitric oxide (NO) .....	10102-43-9	
Nitrogen dioxide (NO <sub>2</sub> ) .....	10102-44-0	30-786 ppmv

1.2 Applicability. This method is applicable for the determination of NO<sub>x</sub> emissions from nitric acid plants.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

### 2.0 Summary of Method

2.1 A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution; the NO<sub>x</sub>, excluding nitrous oxide (N<sub>2</sub>O), are measured by ultraviolet spectrophotometry.

### 3.0 Definition. [Reserved]

### 4.0 Interferences. [Reserved]

### 5.0 Safety

5.1 This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

5.2.1 Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>). Irritating to eyes, skin, nose, and lungs.

5.2.2 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose,

throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.3 Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 3 mg/m<sup>3</sup> will cause lung damage in uninitiated. 1 mg/m<sup>3</sup> for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

### 6.0 Equipment and Supplies

6.1 Sample Collection. Same as Method 7, Section 6.1.

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Wash Bottle. Polyethylene or glass.

6.2.2 Volumetric Flasks. 100-ml (one for each sample).

6.3 Analysis. The following items are required for analysis:

6.3.1 Volumetric Pipettes. 5-, 10-, 15-, and 20-ml to make standards and sample dilutions.

6.3.2 Volumetric Flasks. 1000- and 100-ml for preparing standards and dilution of samples.

6.3.3 Spectrophotometer. To measure ultraviolet absorbance at 210 nm.

6.3.4 Analytical Balance. To measure to within 0.1 mg.

### 7.0 Reagents and Standards

**Note:** Unless otherwise indicated, all reagents are to conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

7.1 Sample Collection. Same as Method 7, Section 7.1. It is important that the amount of hydrogen peroxide in the absorbing solution not be increased. Higher concentrations of peroxide may interfere with sample analysis.

7.2 Sample Recovery. Same as Method 7, Section 7.2.

7.3 Analysis. Same as Method 7, Sections 7.3.1, 7.3.3, and 7.3.4, with the addition of the following:

7.3.1 Working Standard KNO<sub>3</sub> Solution. Dilute 10 ml of the standard solution to 1000 ml with water. One milliliter of the working standard is equivalent to 10 µg NO<sub>2</sub>.

### 8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sample Collection. Same as Method 7, Section 8.1.

8.2 Sample Recovery.

8.2.1 Let the flask sit for a minimum of 16 hours, and then shake the contents for 2 minutes.

8.2.2 Connect the flask to a mercury filled U-tube manometer. Open the valve from the flask to the manometer, and record the flask temperature (T<sub>f</sub>), the barometric pressure, and the difference between the mercury levels in the manometer. The absolute internal pressure in the flask (P<sub>f</sub>) is the barometric pressure less the manometer reading.

8.2.3 Transfer the contents of the flask to a leak-free wash bottle. Rinse the flask three times with 10-ml portions of water, and add to the bottle. Mark the height of the liquid level so that the container can be checked for leakage after transport. Label the container to identify clearly its contents. Seal the container for shipping.

### 9.0 Quality Control

Section	Quality control measure	Effect
10.1 .....	Spectrophotometer calibration .....	Ensures linearity of spectrophotometer response to standards.
11.4 .....	Audit sample analysis .....	Evaluates analytical technique and preparation of standards.

#### 10.0 Calibration and Standardizations

Same as Method 7, Sections 10.2 through 10.5, with the addition of the following:

10.1 Determination of Spectrophotometer Standard Curve. Add 0 ml, 5 ml, 10 ml, 15 ml, and 20 ml of the KNO<sub>3</sub> working standard solution (1 ml = 10 µg NO<sub>2</sub>) to a series of five 100-ml volumetric flasks. To each flask, add 5 ml of absorbing solution. Dilute to the mark with water. The resulting solutions contain 0.0, 50, 100, 150, and 200 µg NO<sub>2</sub>, respectively.

Measure the absorbance by ultraviolet spectrophotometry at 210 nm, using the blank as a zero reference. Prepare a standard curve plotting absorbance vs. µg NO<sub>2</sub>.

**Note:** If other than a 20-ml aliquot of sample is used for analysis, then the amount of absorbing solution in the blank and standards must be adjusted such that the same amount of absorbing solution is in the blank and standards as is in the aliquot of sample used.

10.1.1 Calculate the spectrophotometer calibration factor as follows:

$$K_c = 50 \frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^2 + A_2^2 + A_3^2 + A_4^2} \quad \text{Eq. 7B-2}$$

$$K_c = \frac{\sum_{i=1}^n M_i A_i}{\sum_{i=1}^n A_i^2} \quad \text{Eq. 7B-1}$$

Where:

M<sub>i</sub> = Mass of NO<sub>2</sub> in standard i, µg.

A<sub>i</sub> = Absorbance of NO<sub>2</sub> standard i.

n = Total number of calibration standards.

10.1.2 For the set of calibration standards specified here, Equation 7B-1 simplifies to the following:

10.2 Spectrophotometer Calibration Quality Control. Multiply the absorbance value obtained for each standard by the K<sub>c</sub> factor (reciprocal of the least squares slope) to determine the distance each calibration point lies from the theoretical calibration line. The difference between the calculated concentration values and the actual concentrations (*i.e.*, 50, 100, 150, and 200 µg NO<sub>2</sub>) should be less than 7 percent for all standards.

#### 11.0 Analytical Procedures

11.1 Sample Loss Check. Note the level of the liquid in the container, and confirm whether any sample was lost during shipment. Note this on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.2 Sample Preparation. Immediately prior to analysis, transfer the contents of the shipping container to a 100-ml volumetric flask, and rinse the container twice with 5-ml portions of water. Add the rinse water to the flask, and dilute to mark with water.

11.3 Sample Analysis. Mix the contents of the flask thoroughly and pipette a 20 ml-aliquot of sample into a 100-ml volumetric flask. Dilute to the mark with water. Using the blank as

zero reference, read the absorbance of the sample at 210 nm.

11.4 Audit Sample Analysis. Same as Method 7, Section 11.4, except that a set of audit samples must be analyzed with each set of compliance samples or once per analysis day, or once per week when averaging continuous samples.

#### 12.0 Data Analysis and Calculations

Same as Method 7, Section 12.0, except replace Section 12.3 with the following:

12.1 Total µg NO<sub>2</sub> Per Sample.

$$m = 5 K_c A F \quad \text{Eq. 7B-3}$$

Where:

5 = 100/20, the aliquot factor.

**Note:** If other than a 20-ml aliquot is used for analysis, the factor 5 must be replaced by a corresponding factor.

#### 13.0 Method Performance

13.1 Range. The analytical range of the method as outlined has been determined to be 57 to 1500 milligrams NO<sub>x</sub> (as NO<sub>2</sub>) per dry standard cubic meter, or 30 to 786 parts per million by volume (ppmv) NO<sub>x</sub>.

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

#### 16.0 References

1. National Institute for Occupational Safety and Health. Recommendations for

Occupational Exposure to Nitric Acid. In: Occupational Safety and Health Reporter. Washington, D.C. Bureau of National Affairs, Inc. 1976. p. 149.

2. Rennie, P.J., A.M. Sumner, and F.B. Basketter. Determination of Nitrate in Raw, Potable, and Waste Waters by Ultraviolet Spectrophotometry. *Analyst*. 104:837. September 1979.

17.0 Tables, Diagrams, Flowcharts, and Validation Data. [Reserved]

#### Method 7C—Determination of Nitrogen Oxide Emissions From Stationary Sources (Alkaline Permanganate/Colorimetric Method)

**Note:** This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 3, Method 6 and Method 7.

#### 1.0 Scope and Application

1.1 Analytes.

Analyte	CAS no.	Sensitivity
Nitrogen oxides (NO <sub>x</sub> ), as NO <sub>2</sub> , including:		
Nitric oxide (NO) .....	10102-43-9	ppmv
Nitrogen dioxide (NO <sub>2</sub> ) .....	10102-44-07	

1.2 Applicability. This method applies to the measurement of NO<sub>x</sub> emissions from fossil-fuel fired steam generators, electric utility plants, nitric acid plants, or other sources as specified in the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

## 2.0 Summary of Method

An integrated gas sample is extracted from the stack and passed through impingers containing an alkaline potassium permanganate solution; NO<sub>x</sub> (NO + NO<sub>2</sub>) emissions are oxidized to NO<sub>2</sub> and NO<sub>3</sub>. Then NO<sub>3</sub><sup>-</sup> is reduced to NO<sub>2</sub><sup>-</sup> with cadmium, and the NO<sub>2</sub><sup>-</sup> is analyzed colorimetrically.

## 3.0 Definitions. [Reserved]

## 4.0 Interferences

Possible interferents are sulfur dioxides (SO<sub>2</sub>) and ammonia (NH<sub>3</sub>).

4.1 High concentrations of SO<sub>2</sub> could interfere because SO<sub>2</sub> consumes MnO<sub>4</sub> (as does NO<sub>x</sub>) and, therefore, could reduce the NO<sub>x</sub> collection efficiency. However, when sampling emissions from a coal-fired electric utility plant burning 2.1 percent sulfur coal with no control of SO<sub>2</sub> emissions, collection efficiency was not reduced. In fact, calculations show that sampling 3000 ppm SO<sub>2</sub> will reduce the MnO<sub>4</sub> concentration by only 5 percent if all the SO<sub>2</sub> is consumed in the first impinger.

4.2 Ammonia (NH<sub>3</sub>) is slowly oxidized to NO<sub>3</sub><sup>-</sup> by the absorbing solution. At 100 ppm NH<sub>3</sub> in the gas stream, an interference of 6 ppm NO<sub>x</sub> (11 mg NO<sub>2</sub>/m<sup>3</sup>) was observed when the sample was analyzed 10 days after collection. Therefore, the method may not be applicable to plants using NH<sub>3</sub> injection to control NO<sub>x</sub> emissions unless means are taken to correct the results. An equation has been developed to allow quantification of the interference and is discussed in Reference 5 of Section 16.0.

## 5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety

and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrochloric Acid (HCl). Highly toxic and corrosive. Causes severe damage to skin. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to vapor concentrations of 0.13 to 0.2 percent can be lethal in minutes. Will react with metals, producing hydrogen.

5.2.2 Oxalic Acid (COOH)<sub>2</sub>. Poisonous. Irritating to eyes, skin, nose, and throat.

5.2.3 Sodium Hydroxide (NaOH). Causes severe damage to eye tissues and to skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with small amounts of water.

5.2.4 Potassium Permanganate (KMnO<sub>4</sub>). Caustic, strong oxidizer. Avoid bodily contact with.

## 6.0 Equipment and Supplies

6.1 Sample Collection and Sample Recovery. A schematic of the Method 7C sampling train is shown in Figure 7C-1, and component parts are discussed below. Alternative apparatus and procedures are allowed provided acceptable accuracy and precision can be demonstrated to the satisfaction of the Administrator.

6.1.1 Probe. Borosilicate glass tubing, sufficiently heated to prevent water condensation and equipped with an in-stack or heated out-of-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose). Stainless steel or Teflon tubing may also be used for the probe.

6.1.2 Impingers. Three restricted-orifice glass impingers, having the specifications given in Figure 7C-2, are required for each sampling train. The impingers must be connected in series with leak-free glass connectors. Stopcock grease may be used, if necessary, to prevent leakage. (The

impingers can be fabricated by a glass blower if not available commercially.)

6.1.3 Glass Wool, Stopcock Grease, Drying Tube, Valve, Pump, Barometer, and Vacuum Gauge and Rotameter. Same as in Method 6, Sections 6.1.1.3, 6.1.1.4, 6.1.1.6, 6.1.1.7, 6.1.1.8, 6.1.2, and 6.1.3, respectively.

6.1.4 Rate Meter. Rotameter, or equivalent, accurate to within 2 percent at the selected flow rate of between 400 and 500 ml/min (0.014 to 0.018 cfm). For rotameters, a range of 0 to 1 liter/min (0 to 0.035 cfm) is recommended.

6.1.5 Volume Meter. Dry gas meter (DGM) capable of measuring the sample volume under the sampling conditions of 400 to 500 ml/min (0.014 to 0.018 cfm) for 60 minutes within an accuracy of 2 percent.

6.1.6 Filter. To remove NO<sub>x</sub> from ambient air, prepared by adding 20 g of 5-angstrom molecular sieve to a cylindrical tube (e.g., a polyethylene drying tube).

6.1.7 Polyethylene Bottles. 1-liter, for sample recovery.

6.1.8 Funnel and Stirring Rods. For sample recovery.

## 6.2 Sample Preparation and Analysis.

6.2.1 Hot Plate. Stirring type with 50- by 10-mm Teflon-coated stirring bars.

6.2.2 Beakers. 400-, 600-, and 1000-ml capacities.

6.2.3 Filtering Flask. 500-ml capacity with side arm.

6.2.4 Buchner Funnel. 75-mm ID, with spout equipped with a 13-mm ID by 90-mm long piece of Teflon tubing to minimize possibility of aspirating sample solution during filtration.

6.2.5 Filter Paper. Whatman GF/C, 7.0-cm diameter.

6.2.6 Stirring Rods.

6.2.7 Volumetric Flasks. 100-, 200- or 250-, 500-, and 1000-ml capacity.

6.2.8 Watch Glasses. To cover 600- and 1000-ml beakers.

6.2.9 Graduated Cylinders. 50- and 250-ml capacities.

6.2.10 Pipettes. Class A.

6.2.11 pH Meter. To measure pH from 0.5 to 12.0.

6.2.12 Burette. 50-ml with a micrometer type stopcock. (The stopcock is Catalog No. 8225-t-05, Ace Glass, Inc., Post Office Box 996, Louisville, Kentucky 50201.) Place a glass wool plug in bottom of burette. Cut off burette at a height of 43 cm (17 in.)

from the top of plug, and have a blower attach a glass funnel to top of burette such that the diameter of the burette remains essentially unchanged. Other means of attaching the funnel are acceptable.

6.2.13 Glass Funnel. 75-mm ID at the top.

6.2.14 Spectrophotometer. Capable of measuring absorbance at 540 nm; 1-cm cells are adequate.

6.2.15 Metal Thermometers. Bimetallic thermometers, range 0 to 150 °C (32 to 300 °F).

6.2.16 Culture Tubes. 20-by 150-mm, Kimax No. 45048.

6.2.17 Parafilm "M." Obtained from American Can Company, Greenwich, Connecticut 06830.

6.2.18 CO<sub>2</sub> Measurement Equipment. Same as in Method 3, Section 6.0.

## 7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

### 7.1 Sample Collection.

7.1.1 Water. Deionized distilled to conform to ASTM Specification D 1193-77 or 91 Type 3 (incorporated by reference—see § 60.17).

7.1.2 Potassium Permanganate, 4.0 Percent (w/w), Sodium Hydroxide, 2.0 Percent (w/w) solution (KMnO<sub>4</sub>/NaOH solution). Dissolve 40.0 g of KMnO<sub>4</sub> and 20.0 g of NaOH in 940 ml of water.

### 7.2 Sample Preparation and Analysis.

7.2.1 Water. Same as in Section 7.1.1.

7.2.2 Oxalic Acid Solution. Dissolve 48 g of oxalic acid [(COOH)<sub>2</sub>·2H<sub>2</sub>O] in water, and dilute to 500 ml. Do not heat the solution.

7.2.3 Sodium Hydroxide, 0.5 N. Dissolve 20 g of NaOH in water, and dilute to 1 liter.

7.2.4 Sodium Hydroxide, 10 N. Dissolve 40 g of NaOH in water, and dilute to 100 ml.

7.2.5 Ethylenediamine Tetraacetic Acid (EDTA) Solution, 6.5 percent (w/v). Dissolve 6.5 g of EDTA (disodium salt) in water, and dilute to 100 ml. Dissolution is best accomplished by using a magnetic stirrer.

7.2.6 Column Rinse Solution. Add 20 ml of 6.5 percent EDTA solution to 960 ml of water, and adjust the pH to between 11.7 and 12.0 with 0.5 N NaOH.

7.2.7 Hydrochloric Acid (HCl), 2 N. Add 86 ml of concentrated HCl to a 500 ml-volumetric flask containing water,

dilute to volume, and mix well. Store in a glass-stoppered bottle.

7.2.8 Sulfanilamide Solution. Add 20 g of sulfanilamide (melting point 165 to 167 °C (329 to 333 °F)) to 700 ml of water. Add, with mixing, 50 ml concentrated phosphoric acid (85 percent), and dilute to 1000 ml. This solution is stable for at least 1 month, if refrigerated.

7.2.9 N-(1-Naphthyl)-Ethylenediamine Dihydrochloride (NEDA) Solution. Dissolve 0.5 g of NEDA in 500 ml of water. An aqueous solution should have one absorption peak at 320 nm over the range of 260 to 400 nm. NEDA that shows more than one absorption peak over this range is impure and should not be used. This solution is stable for at least 1 month if protected from light and refrigerated.

7.2.10 Cadmium. Obtained from Matheson Coleman and Bell, 2909 Highland Avenue, Norwood, Ohio 45212, as EM Laboratories Catalog No. 2001. Prepare by rinsing in 2 N HCl for 5 minutes until the color is silver-grey. Then rinse the cadmium with water until the rinsings are neutral when tested with pH paper. CAUTION: H<sub>2</sub> is liberated during preparation. Prepare in an exhaust hood away from any flame or combustion source.

7.2.11 Sodium Sulfite (NaNO<sub>2</sub>) Standard Solution, Nominal Concentration, 1000 µg NO<sub>2</sub><sup>-</sup>/ml. Desiccate NaNO<sub>2</sub> overnight. Accurately weigh 1.4 to 1.6 g of NaNO<sub>2</sub> (assay of 97 percent NaNO<sub>2</sub> or greater), dissolve in water, and dilute to 1 liter. Calculate the exact NO<sub>2</sub><sup>-</sup> concentration using Equation 7C-1 in Section 12.2. This solution is stable for at least 6 months under laboratory conditions.

7.2.12 Potassium Nitrate (KNO<sub>3</sub>) Standard Solution. Dry KNO<sub>3</sub> at 110 °C (230 °F) for 2 hours, and cool in a desiccator. Accurately weigh 9 to 10 g of KNO<sub>3</sub> to within 0.1 mg, dissolve in water, and dilute to 1 liter. Calculate the exact NO<sub>3</sub><sup>-</sup> concentration using Equation 7C-2 in Section 12.3. This solution is stable for 2 months without preservative under laboratory conditions.

7.2.13 Spiking Solution. Pipette 7 ml of the KNO<sub>3</sub> standard into a 100-ml volumetric flask, and dilute to volume.

7.2.14 Blank Solution. Dissolve 2.4 g of KMnO<sub>4</sub> and 1.2 g of NaOH in 96 ml of water. Alternatively, dilute 60 ml of KMnO<sub>4</sub>/NaOH solution to 100 ml.

7.2.15 Quality Assurance Audit Samples. Same as in Method 7, Section 7.3.10. When requesting audit samples, specify that they be in the appropriate concentration range for Method 7C.

## 8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Preparation of Sampling Train. Add 200 ml of KMnO<sub>4</sub>/NaOH solution (Section 7.1.2) to each of three impingers, and assemble the train as shown in Figure 7C-1. Adjust the probe heater to a temperature sufficient to prevent water condensation.

8.2 Leak-Checks. Same as in Method 6, Section 8.2.

### 8.3 Sample Collection.

8.3.1 Record the initial DGM reading and barometric pressure. Determine the sampling point or points according to the appropriate regulations (e.g., § 60.46(b)(5) of 40 CFR Part 60). Position the tip of the probe at the sampling point, connect the probe to the first impinger, and start the pump. Adjust the sample flow to a value between 400 and 500 ml/min (0.014 and 0.018 cfm). CAUTION: DO NOT EXCEED THESE FLOW RATES. Once adjusted, maintain a constant flow rate during the entire sampling run. Sample for 60 minutes. For relative accuracy (RA) testing of continuous emission monitors, the minimum sampling time is 1 hour, sampling 20 minutes at each traverse point.

**Note:** When the SO<sub>2</sub> concentration is greater than 1200 ppm, the sampling time may have to be reduced to 30 minutes to eliminate plugging of the impinger orifice with MnO<sub>2</sub>. For RA tests with SO<sub>2</sub> greater than 1200 ppm, sample for 30 minutes (10 minutes at each point).

8.3.2 Record the DGM temperature, and check the flow rate at least every 5 minutes. At the conclusion of each run, turn off the pump, remove the probe from the stack, and record the final readings. Divide the sample volume by the sampling time to determine the average flow rate. Conduct the mandatory post-test leak-check. If a leak is found, void the test run, or use procedures acceptable to the Administrator to adjust the sample volume for the leakage.

8.4 CO<sub>2</sub> Measurement. During sampling, measure the CO<sub>2</sub> content of the stack gas near the sampling point using Method 3. The single-point grab sampling procedure is adequate, provided the measurements are made at least three times (near the start, midway, and before the end of a run), and the average CO<sub>2</sub> concentration is computed. The Orsat or Fyrite analyzer may be used for this analysis.

8.5 Sample Recovery. Disconnect the impingers. Pour the contents of the impingers into a 1-liter polyethylene bottle using a funnel and a stirring rod (or other means) to prevent spillage. Complete the quantitative transfer by

rinsing the impingers and connecting tubes with water until the rinsings are

clear to light pink, and add the rinsings to the bottle. Mix the sample, and mark

the solution level. Seal and identify the sample container.

### 9.0 Quality Control

Section	Quality control measure	Effect
8.2, 10.1–10.3 .....	Sampling equipment leak-check and calibration.	Ensure accurate measurement of sample volume.
10.4 .....	Spectrophotometer calibration .....	Ensure linearity of spectrophotometer response to standards.
11.3 .....	Spiked sample analysis .....	Ensure reduction efficiency of column.
11.6 .....	Audit sample analysis .....	Evaluate analytical technique, preparation of standards.

### 10.0 Calibration and Standardizations

10.1 Volume Metering System. Same as Method 6, Section 10.1. For detailed instructions on carrying out these calibrations, it is suggested that Section 3.5.2 of Reference 4 of Section 16.0 be consulted.

10.2 Temperature Sensors and Barometer. Same as in Method 6, Sections 10.2 and 10.4, respectively.

10.3 Check of Rate Meter Calibration Accuracy (Optional). Disconnect the probe from the first impinger, and connect the filter. Start the pump, and adjust the rate meter to read between 400 and 500 ml/min (0.014 and 0.018 cfm). After the flow rate has stabilized, start measuring the volume sampled, as recorded by the dry gas meter and the sampling time. Collect enough volume to measure accurately the flow rate. Then calculate the flow rate. This average flow rate must be less than 500 ml/min (0.018 cfm) for the sample to be valid; therefore, it is recommended that the flow rate be checked as above prior to each test.

#### 10.4 Spectrophotometer.

10.4.1 Dilute 5.0 ml of the  $\text{NaNO}_2$  standard solution to 200 ml with water. This solution nominally contains 25  $\mu\text{g NO}_2^-/\text{ml}$ . Use this solution to prepare calibration standards to cover the range of 0.25 to 3.00  $\mu\text{g NO}_2^-/\text{ml}$ . Prepare a minimum of three standards each for the linear and slightly nonlinear (described below) range of the curve. Use pipettes for all additions.

10.4.2 Measure the absorbance of the standards and a water blank as instructed in Section 11.5. Plot the net absorbance vs.  $\mu\text{g NO}_2^-/\text{ml}$ . Draw a smooth curve through the points. The curve should be linear up to an absorbance of approximately 1.2 with a slope of approximately 0.53 absorbance units/ $\mu\text{g NO}_2^-/\text{ml}$ . The curve should pass through the origin. The curve is slightly nonlinear from an absorbance of 1.2 to 1.6.

### 11.0 Analytical Procedures

11.1 Sample Stability. Collected samples are stable for at least four

weeks; thus, analysis must occur within 4 weeks of collection.

#### 11.2 Sample Preparation.

11.2.1 Prepare a cadmium reduction column as follows: Fill the burette with water. Add freshly prepared cadmium slowly, with tapping, until no further settling occurs. The height of the cadmium column should be 39 cm (15 in). When not in use, store the column under rinse solution.

**Note:** The column should not contain any bands of cadmium fines. This may occur if regenerated cadmium is used and will greatly reduce the column lifetime.

11.2.2 Note the level of liquid in the sample container, and determine whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, the volume lost can be determined from the difference between initial and final solution levels, and this value can then be used to correct the analytical result. Quantitatively transfer the contents to a 1-liter volumetric flask, and dilute to volume.

11.2.3 Take a 100-ml aliquot of the sample and blank (unexposed  $\text{KMnO}_4/\text{NaOH}$ ) solutions, and transfer to 400-ml beakers containing magnetic stirring bars. Using a pH meter, add concentrated  $\text{H}_2\text{SO}_4$  with stirring until a pH of 0.7 is obtained. Allow the solutions to stand for 15 minutes. Cover the beakers with watch glasses, and bring the temperature of the solutions to 50 °C (122 °F). Keep the temperature below 60 °C (140 °F). Dissolve 4.8 g of oxalic acid in a minimum volume of water, approximately 50 ml, at room temperature. Do not heat the solution. Add this solution slowly, in increments, until the  $\text{KMnO}_4$  solution becomes colorless. If the color is not completely removed, prepare some more of the above oxalic acid solution, and add until a colorless solution is obtained. Add an excess of oxalic acid by dissolving 1.6 g of oxalic acid in 50 ml of water, and add 6 ml of this solution to the colorless solution. If suspended matter is present, add concentrated  $\text{H}_2\text{SO}_4$  until a clear solution is obtained.

11.2.4 Allow the samples to cool to near room temperature, being sure that the samples are still clear. Adjust the pH to between 11.7 and 12.0 with 10 N  $\text{NaOH}$ . Quantitatively transfer the mixture to a Buchner funnel containing GF/C filter paper, and filter the precipitate. Filter the mixture into a 500-ml filtering flask. Wash the solid material four times with water. When filtration is complete, wash the Teflon tubing, quantitatively transfer the filtrate to a 500-ml volumetric flask, and dilute to volume. The samples are now ready for cadmium reduction. Pipette a 50-ml aliquot of the sample into a 150-ml beaker, and add a magnetic stirring bar. Pipette in 1.0 ml of 6.5 percent EDTA solution, and mix.

11.3 Determine the correct stopcock setting to establish a flow rate of 7 to 9 ml/min of column rinse solution through the cadmium reduction column. Use a 50-ml graduated cylinder to collect and measure the solution volume. After the last of the rinse solution has passed from the funnel into the burette, but before air entrapment can occur, start adding the sample, and collect it in a 250-ml graduated cylinder. Complete the quantitative transfer of the sample to the column as the sample passes through the column. After the last of the sample has passed from the funnel into the burette, start adding 60 ml of column rinse solution, and collect the rinse solution until the solution just disappears from the funnel. Quantitatively transfer the sample to a 200-ml volumetric flask (a 250-ml flask may be required), and dilute to volume. The samples are now ready for  $\text{NO}_2^-$  analysis.

**Note:** Two spiked samples should be run with every group of samples passed through the column. To do this, prepare two additional 50-ml aliquots of the sample suspected to have the highest  $\text{NO}_2^-$  concentration, and add 1 ml of the spiking solution to these aliquots. If the spike recovery or column efficiency (see Section 12.2) is below 95 percent, prepare a new column, and repeat the cadmium reduction.

11.4 Repeat the procedures outlined in Sections 11.2 and 11.3 for each sample and each blank.

11.5 Sample Analysis. Pipette 10 ml of sample into a culture tube. Pipette in 10 ml of sulfanilamide solution and 1.4 ml of NEDA solution. Cover the culture tube with parafilm, and mix the solution. Prepare a blank in the same manner using the sample from treatment of the unexposed KMnO<sub>4</sub>/NaOH solution. Also, prepare a calibration standard to check the slope of the calibration curve. After a 10-minute color development interval, measure the absorbance at 540 nm against water. Read µg NO<sub>2</sub><sup>-</sup>/ml from the calibration curve. If the absorbance is greater than that of the highest calibration standard, use less than 10 ml of sample, and repeat the analysis. Determine the NO<sub>2</sub><sup>-</sup> concentration using the calibration curve obtained in Section 10.4.

**Note:** Some test tubes give a high blank NO<sub>2</sub><sup>-</sup> value but culture tubes do not.

11.6 Audit Sample Analysis. Same as in Method 7, Section 11.4.

#### 12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

#### 12.1 Nomenclature.

B = Analysis of blank, µg NO<sub>2</sub><sup>-</sup>/ml.

C = Concentration of NO<sub>x</sub> as NO<sub>2</sub>, dry basis, mg/dsm<sup>3</sup>.

E = Column efficiency, dimensionless

K<sub>2</sub> = 10<sup>-3</sup> mg/µg.

m = Mass of NO<sub>x</sub>, as NO<sub>2</sub>, in sample,

µg.

P<sub>bar</sub> = Barometric pressure, mm Hg (in.

Hg).

P<sub>std</sub> = Standard absolute pressure, 760

mm Hg (29.92 in. Hg).

s = Concentration of spiking solution, µg

NO<sub>3</sub>/ml.

S = Analysis of sample, µg NO<sub>2</sub><sup>-</sup>/ml.

T<sub>m</sub> = Average dry gas meter absolute temperature, °K.

T<sub>std</sub> = Standard absolute temperature, 293 °K (528 °R).

V<sub>m(std)</sub> = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

V<sub>m</sub> = Dry gas volume as measured by the dry gas meter, scm (scf).

x = Analysis of spiked sample, µg NO<sub>2</sub><sup>-</sup>/ml.

X = Correction factor for CO<sub>2</sub> collection = 100/(100 - %CO<sub>2</sub>(V/V)).

y = Analysis of unspiked sample, µg NO<sub>2</sub><sup>-</sup>/ml.

Y = Dry gas meter calibration factor.

1.0 ppm NO = 1.247 mg NO/m<sup>3</sup> at STP.

1.0 ppm NO<sub>2</sub> = 1.912 mg NO<sub>2</sub>/m<sup>3</sup> at STP.

1 ft<sup>3</sup> = 2.832 × 10<sup>-2</sup> m<sup>3</sup>.

12.2 NO<sub>2</sub> Concentration. Calculate the NO<sub>2</sub> concentration of the solution (see Section 7.2.11) using the following equation:

$$\frac{\mu\text{g NO}_2^-}{\text{ml}} = \text{g NaNO}_2 \times \frac{\text{purity, \%}}{100} \times 10^3 \times \frac{46.01}{69.01} \quad \text{Eq. 7C-1}$$

12.3 NO<sub>3</sub> Concentration. Calculate the NO<sub>3</sub> concentration of the KNO<sub>3</sub> solution (see Section 7.2.12) using the following equation:

$$\frac{\mu\text{g NO}_3^-}{\text{ml}} = \text{g KNO}_3 \times (10^3) \times \frac{62.01}{101.10} \quad \text{Eq. 7C-2}$$

12.4 Sample Volume, Dry Basis, Corrected to Standard Conditions.

$$V_{m(\text{std})} = V_m \times Y \times \frac{T_{\text{std}}}{T_m} \times \frac{P_{\text{bar}}}{P_{\text{std}}} \quad \text{Eq. 7C-3}$$

$$= K_1 \times Y \times V_m \times \frac{P_{\text{bar}}}{T_m}$$

Where:

K<sub>1</sub> = 0.3855 °K/mm Hg for metric units.

K<sub>1</sub> = 17.65 °R/in. Hg for English units.

12.5 Efficiency of Cadmium Reduction Column. Calculate this value as follows:

$$E = \frac{200(x-y)}{1.0s \times \frac{46.01}{62.01}} = \frac{269.6(x-y)}{s} \quad \text{Eq. 7C-4}$$

Where:

200 = Final volume of sample and blank after passing through the column, ml.

1.0 = Volume of spiking solution added, ml.

46.01 = µg NO<sub>2</sub><sup>-</sup>/µmole.

62.01 = µg NO<sub>3</sub><sup>-</sup>/µmole.

12.6 Total µg NO<sub>2</sub>.

$$m = 200 \left( \frac{500}{50} \right) \left( \frac{1000}{100} \right) \left( \frac{(S-B)}{E} \right) = \frac{(2 \times 10^4)(S-B)}{E} \quad \text{Eq. 7C-5}$$

Where:

500 = Total volume of prepared sample, ml.

50 = Aliquot of prepared sample processed through cadmium column, ml.

100 = Aliquot of KMnO<sub>4</sub>/NaOH solution, ml.

1000 = Total volume of  $\text{KMnO}_4/\text{NaOH}$  solution, ml.

#### 12.7 Sample Concentration.

$$C = K_2 \frac{m}{V_{m(\text{std})}} \quad \text{Eq. 7C-6}$$

#### 13.0 Method Performance

13.1 Precision. The intra-laboratory relative standard deviation for a single measurement is 2.8 and 2.9 percent at 201 and 268 ppm  $\text{NO}_x$ , respectively.

13.2 Bias. The method does not exhibit any bias relative to Method 7.

13.3 Range. The lower detectable limit is 13 mg  $\text{NO}_x/\text{m}^3$ , as  $\text{NO}_2$  (7 ppm  $\text{NO}_x$ ) when sampling at 500 ml/min for 1 hour. No upper limit has been established; however, when using the recommended sampling conditions, the

method has been found to collect  $\text{NO}_x$  emissions quantitatively up to 1782 mg  $\text{NO}_x/\text{m}^3$ , as  $\text{NO}_2$  (932 ppm  $\text{NO}_x$ ).

#### 14.0 Pollution Prevention. [Reserved]

#### 15.0 Waste Management. [Reserved]

#### 16.0 References

1. Margeson, J.H., W.J. Mitchell, J.C. Suggs, and M.R. Midgett. Integrated Sampling and Analysis Methods for Determining  $\text{NO}_x$  Emissions at Electric Utility Plants. U.S. Environmental Protection Agency, Research Triangle Park, NC. Journal of the Air Pollution Control Association. 32:1210–1215. 1982.

2. Memorandum and attachment from J.H. Margeson, Source Branch, Quality Assurance

Division, Environmental Monitoring Systems Laboratory, to The Record, EPA. March 30, 1983.  $\text{NH}_3$  Interference in Methods 7C and 7D.

3. Margeson, J.H., J.C. Suggs, and M.R. Midgett. Reduction of Nitrate to Nitrite with Cadmium. Anal. Chem. 52:1955–57. 1980.

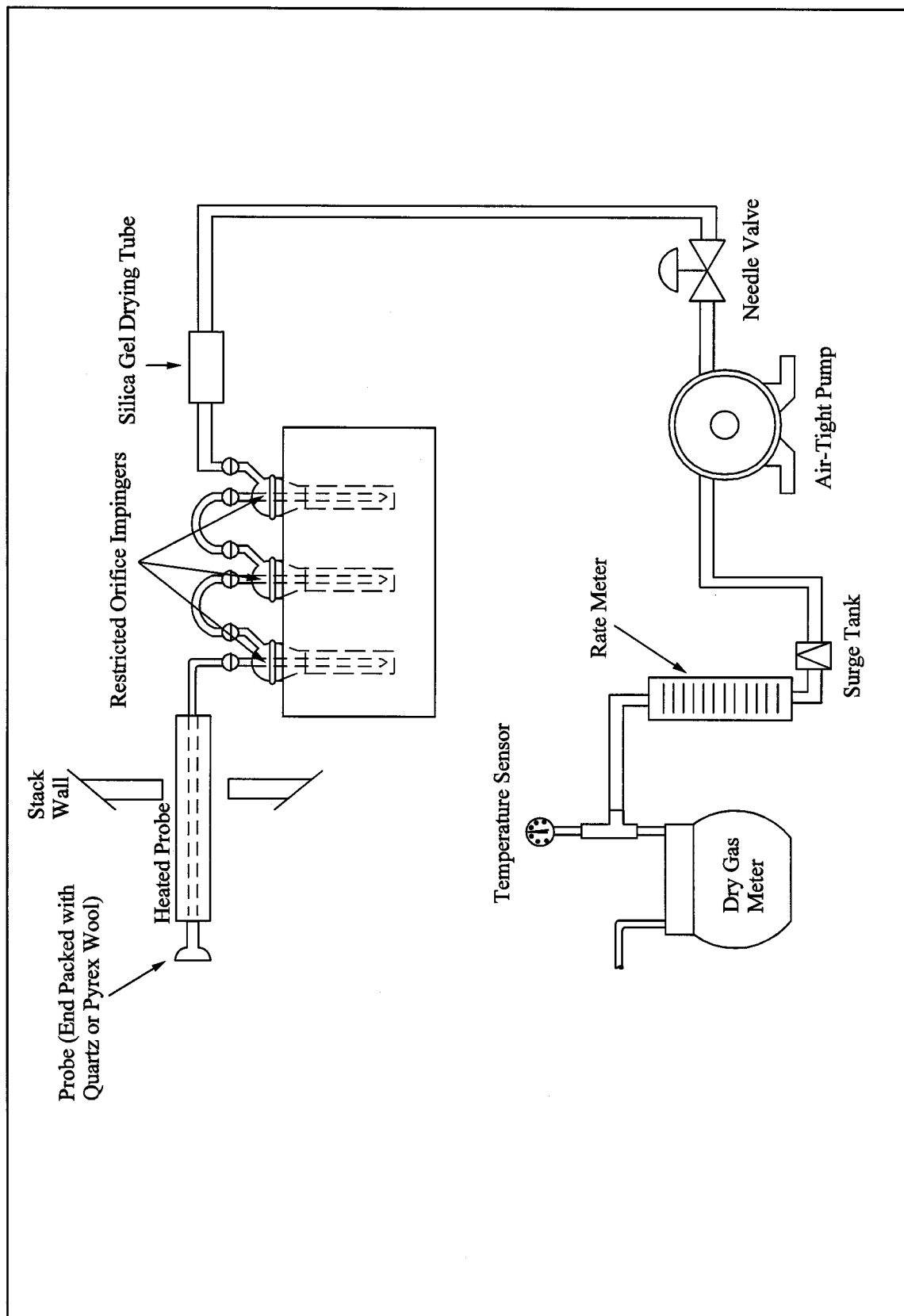
4. Quality Assurance Handbook for Air Pollution Measurement Systems. Volume III—Stationary Source Specific Methods. U.S. Environmental Protection Agency. Research Triangle Park, NC. Publication No. EPA-600/4-77-027b. August 1977.

5. Margeson, J.H., *et al.* An Integrated Method for Determining  $\text{NO}_x$  Emissions at Nitric Acid Plants. Analytical Chemistry. 47 (11):1801. 1975.

**BILLING CODE 6560-50-P**



## 17.0 Tables, Diagrams, Flowcharts, and Validation Data

Figure 7C-1. NO<sub>x</sub> Sampling Train.

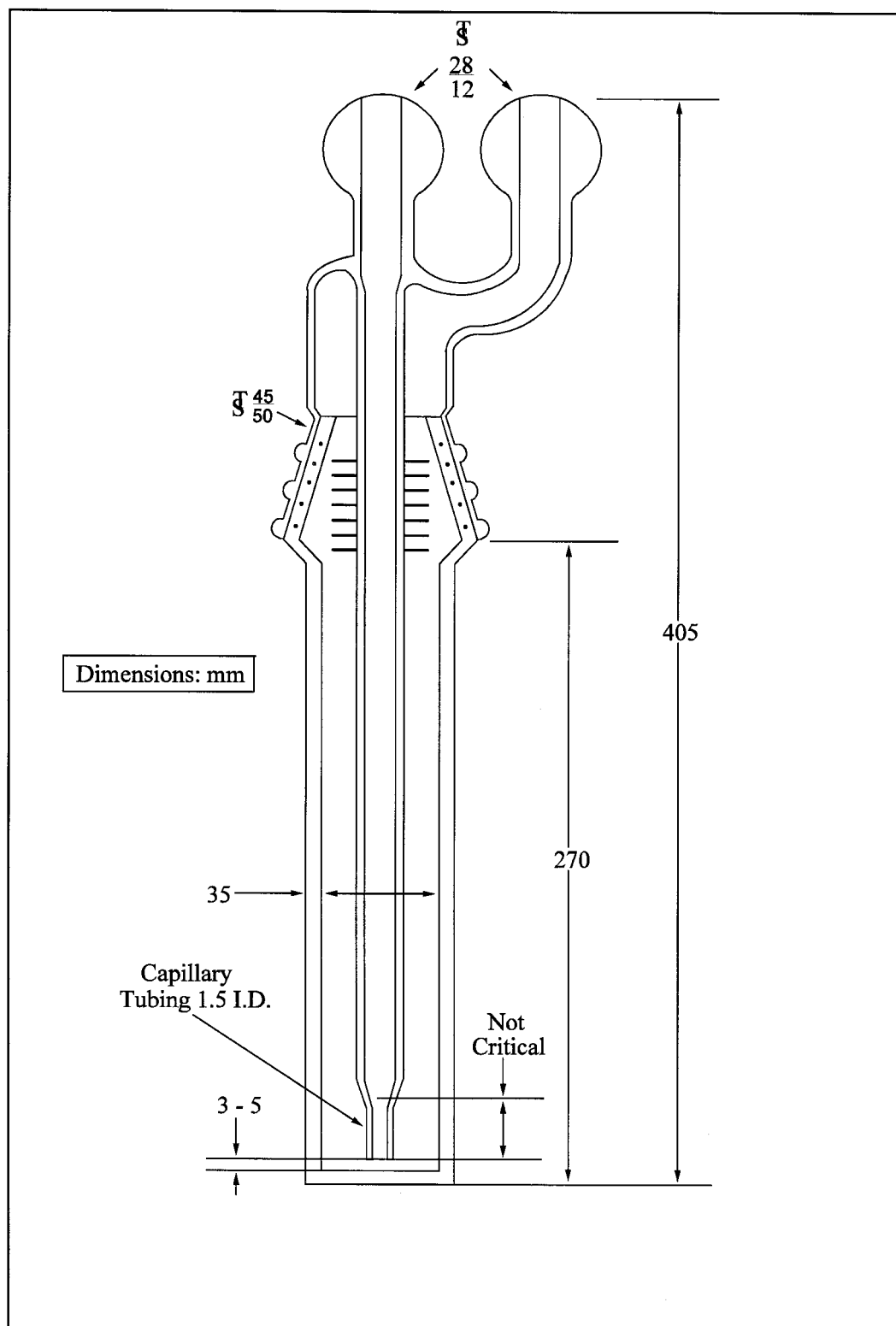


Figure 7C-2. Restricted-Orifice Impinger.

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**Method 7D—Determination of Nitrogen Oxide Emissions From Stationary Sources (Alkaline-Permanganate/Ion Chromatographic Method)**

**Note:** This method is not inclusive with respect to specifications (e.g., equipment and

supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test

methods: Method 1, Method 3, Method 6, Method 7, and Method 7C.

**1.0 Scope and Application****1.1 Analytes.**

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO <sub>x</sub> ), as NO <sub>2</sub> , including:		
Nitric oxide (NO) .....	10102-43-9	7 ppmv
Nitrogen dioxide (NO <sub>2</sub> ) .....	10102-44-0	

1.2 Applicability. This method applies to the measurement of NO<sub>x</sub> emissions from fossil-fuel fired steam generators, electric utility plants, nitric acid plants, or other sources as specified in the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

**2.0 Summary of Method**

An integrated gas sample is extracted from the stack and passed through impingers containing an alkaline-potassium permanganate solution; NO<sub>x</sub> (NO + NO<sub>2</sub>) emissions are oxidized to NO<sub>3</sub><sup>-</sup>. Then NO<sub>3</sub><sup>-</sup> is analyzed by ion chromatography.

**3.0 Definitions [Reserved]****4.0 Interferences**

Same as in Method 7C, Section 4.0.

**5.0 Safety**

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>). Irritating to eyes, skin, nose, and lungs. 30% H<sub>2</sub>O<sub>2</sub> is a strong oxidizing agent; avoid contact with skin, eyes, and combustible material. Wear gloves when handling.

5.2.2 Sodium Hydroxide (NaOH). Causes severe damage to eye tissues and to skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.3 Potassium Permanganate (KMnO<sub>4</sub>). Caustic, strong oxidizer. Avoid bodily contact with.

**6.0 Equipment and Supplies**

6.1 Sample Collection and Sample Recovery. Same as Method 7C, Section 6.1. A schematic of the sampling train used in performing this method is shown in Figure 7C-1 of Method 7C.

6.2 Sample Preparation and Analysis.

6.2.1 Magnetic Stirrer. With 25- by 10-mm Teflon-coated stirring bars.

6.2.2 Filtering Flask. 500-ml capacity with sidearm.

6.2.3 Buchner Funnel. 75-mm ID, with spout equipped with a 13-mm ID by 90-mm long piece of Teflon tubing to minimize possibility of aspirating sample solution during filtration.

6.2.4 Filter Paper. Whatman GF/C, 7.0-cm diameter.

6.2.5 Stirring Rods.

6.2.6 Volumetric Flask. 250-ml.

6.2.7 Pipettes. Class A.

6.2.8 Erlenmeyer Flasks. 250-ml.

6.2.9 Ion Chromatograph. Equipped with an anion separator column to separate NO<sub>3</sub><sup>-</sup>, H<sub>3</sub><sup>+</sup> suppressor, and necessary auxiliary equipment. Nonsuppressed and other forms of ion chromatography may also be used provided that adequate resolution of NO<sub>3</sub><sup>-</sup> is obtained. The system must also be able to resolve and detect NO<sub>2</sub><sup>-</sup>.

**7.0 Reagents and Standards**

**Note:** Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

**7.1 Sample Collection.**

7.1.1 Water. Deionized distilled to conform to ASTM specification D 1193-

77 or 91 Type 3 (incorporated by reference—see § 60.17).

7.1.2 Potassium Permanganate, 4.0 Percent (w/w), Sodium Hydroxide, 2.0 Percent (w/w). Dissolve 40.0 g of KMnO<sub>4</sub> and 20.0 g of NaOH in 940 ml of water.

7.2 Sample Preparation and Analysis.

7.2.1 Water. Same as in Section 7.1.1.

7.2.2 Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>), 5 Percent. Dilute 30 percent H<sub>2</sub>O<sub>2</sub> 1:5 (v/v) with water.

7.2.3 Blank Solution. Dissolve 2.4 g of KMnO<sub>4</sub> and 1.2 g of NaOH in 96 ml of water. Alternatively, dilute 60 ml of KMnO<sub>4</sub>/NaOH solution to 100 ml.

7.2.4 KNO<sub>3</sub> Standard Solution. Dry KNO<sub>3</sub> at 110°C for 2 hours, and cool in a desiccator. Accurately weigh 9 to 10 g of KNO<sub>3</sub> to within 0.1 mg, dissolve in water, and dilute to 1 liter. Calculate the exact NO<sub>3</sub><sup>-</sup> concentration using Equation 7D-1 in Section 12.2. This solution is stable for 2 months without preservative under laboratory conditions.

7.2.5 Eluent, 0.003 M NaHCO<sub>3</sub>/0.0024 M Na<sub>2</sub>CO<sub>3</sub>. Dissolve 1.008 g NaHCO<sub>3</sub> and 1.018 g Na<sub>2</sub>CO<sub>3</sub> in water, and dilute to 4 liters. Other eluents capable of resolving nitrate ion from sulfate and other species present may be used.

7.2.6 Quality Assurance Audit Samples. Same as Method 7, Section 7.3.10. When requesting audit samples, specify that they be in the appropriate concentration range for Method 7D.

8.0 Sample Collection, Preservation, Transport, and Storage.

8.1 Sampling. Same as in Method 7C, Section 8.1.

8.2 Sample Recovery. Same as in Method 7C, Section 8.2.

8.3 Sample Preparation for Analysis.

**Note:** Samples must be analyzed within 28 days of collection.

8.3.1 Note the level of liquid in the sample container, and determine whether any sample was lost during shipment. If a noticeable amount of

leakage has occurred, the volume lost can be determined from the difference between initial and final solution levels, and this value can then be used to correct the analytical result.

Quantitatively transfer the contents to a 1-liter volumetric flask, and dilute to volume.

8.3.2 Sample preparation can be started 36 hours after collection. This time is necessary to ensure that all  $\text{NO}_2^-$  is converted to  $\text{NO}_3^-$  in the collection solution. Take a 50-ml aliquot of the sample and blank, and transfer to 250-ml Erlenmeyer flasks. Add a

magnetic stirring bar. Adjust the stirring rate to as fast a rate as possible without loss of solution. Add 5 percent  $\text{H}_2\text{O}_2$  in increments of approximately 5 ml using a 5-ml pipette. When the  $\text{KMnO}_4$  color appears to have been removed, allow the precipitate to settle, and examine the supernatant liquid. If the liquid is clear, the  $\text{H}_2\text{O}_2$  addition is complete. If the  $\text{KMnO}_4$  color persists, add more  $\text{H}_2\text{O}_2$ , with stirring, until the supernatant liquid is clear.

**Note:** The faster the stirring rate, the less volume of  $\text{H}_2\text{O}_2$  that will be required to remove the  $\text{KMnO}_4$ .) Quantitatively transfer

the mixture to a Buchner funnel containing GF/C filter paper, and filter the precipitate. The spout of the Buchner funnel should be equipped with a 13-mm ID by 90-mm long piece of Teflon tubing. This modification minimizes the possibility of aspirating sample solution during filtration. Filter the mixture into a 500-ml filtering flask. Wash the solid material four times with water. When filtration is complete, wash the Teflon tubing, quantitatively transfer the filtrate to a 250-ml volumetric flask, and dilute to volume. The sample and blank are now ready for  $\text{NO}_3^-$  analysis.

## 9.0 Quality Control

Section	Quality control measure	Effect
8.2, 10.1–10.3	Sampling equipment leak-check and calibration.	Ensure accurate measurement of sample volume.
10.4	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards.
11.3	Spiked sample analysis	Ensure reduction efficiency of column.
11.6	Audit sample analysis	Evaluate analytical technique, preparation of standards.

## 10.0 Calibration and Standardizations

### 10.1 Dry Gas Meter (DGM) System.

10.1.1 Initial Calibration. Same as in Method 6, Section 10.1.1. For detailed instructions on carrying out this calibration, it is suggested that Section 3.5.2 of Citation 4 in Section 16.0 of Method 7C be consulted.

10.1.2 Post-Test Calibration Check. Same as in Method 6, Section 10.1.2.

10.2 Thermometers for DGM and Barometer. Same as in Method 6, Sections 10.2 and 10.4, respectively.

### 10.3 Ion Chromatograph.

10.3.1 Dilute a given volume (1.0 ml or greater) of the  $\text{KNO}_3$  standard solution to a convenient volume with water, and use this solution to prepare calibration standards. Prepare at least four standards to cover the range of the samples being analyzed. Use pipettes for all additions. Run standards as instructed in Section 11.2. Determine peak height or area, and plot the

individual values versus concentration in  $\mu\text{g NO}_3^-/\text{ml}$ .

10.3.2 Do not force the curve through zero. Draw a smooth curve through the points. The curve should be linear. With the linear curve, use linear regression to determine the calibration equation.

## 11.0 Analytical Procedures

11.1 The following chromatographic conditions are recommended: 0.003 M  $\text{NaHCO}_3/0.0024 \text{ Na}_2\text{CO}_3$  eluent solution (Section 7.2.5), full scale range, 3  $\mu\text{MHO}$ ; sample loop, 0.5 ml; flow rate, 2.5 ml/min. These conditions should give a  $\text{NO}_3^-$  retention time of approximately 15 minutes (Figure 7D-1).

11.2 Establish a stable baseline. Inject a sample of water, and determine whether any  $\text{NO}_3^-$  appears in the chromatogram. If  $\text{NO}_3^-$  is present, repeat the water load/injection procedure approximately five times;

then re-inject a water sample and observe the chromatogram. When no  $\text{NO}_3^-$  is present, the instrument is ready for use. Inject calibration standards. Then inject samples and a blank. Repeat the injection of the calibration standards (to compensate for any drift in response of the instrument). Measure the  $\text{NO}_3^-$  peak height or peak area, and determine the sample concentration from the calibration curve.

11.3 Audit Analysis. Same as in Method 7, Section 11.4

## 12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Nomenclature. Same as in Method 7C, Section 12.1.

12.2  $\text{NO}_3^-$  concentration. Calculate the  $\text{NO}_3^-$  concentration in the  $\text{KNO}_3$  standard solution (see Section 7.2.4) using the following equation:

$$\frac{\mu\text{g NO}_3^-}{\text{ml}} = \text{g of KNO}_3 \times 10^3 \times \frac{62.01}{101.10} \quad \text{Eq. 7D-1}$$

12.3 Sample Volume, Dry Basis, Corrected to Standard Conditions. Same as in Method 7C, Section 12.4.

12.4 Total  $\mu\text{g NO}_2$  Per Sample.

$$m = 250 \left( \frac{1000}{50} \right) \left( \frac{46.01}{62.01} \right) (S - B) \quad \text{Eq. 7D-2}$$

$$= 3710 (S - B)$$

Where:

250 = Volume of prepared sample, ml.

1000 = Total volume of  $\text{KMnO}_4$  solution, ml.

50 = Aliquot of  $\text{KMnO}_4/\text{NaOH}$  solution, ml.

46.01 = Molecular weight of  $\text{NO}_3^-$ .

62.01 = Molecular weight of  $\text{NO}_3^-$ .

12.5 Sample Concentration. Same as in Method 7C, Section 12.7.

### 13.0 Method Performance

13.1 Precision. The intra-laboratory relative standard deviation for a single measurement is approximately 6 percent at 200 to 270 ppm NO<sub>x</sub>.

13.2 Bias. The method does not exhibit any bias relative to Method 7.

13.3 Range. The lower detectable limit is similar to that of Method 7C. No upper limit has been established; however, when using the recommended sampling conditions, the method has been found to collect NO<sub>x</sub> emissions quantitatively up to 1782 mg NO<sub>x</sub>/m<sup>3</sup>, as NO<sub>2</sub> (932 ppm NO<sub>x</sub>).

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

### 16.0 References

Same as Method 7C, Section 16.0, References 1, 2, 4, and 5.

BILLING CODE 6560-50-P

### 17.0 Tables, Diagrams, Flowcharts, and Validation Data

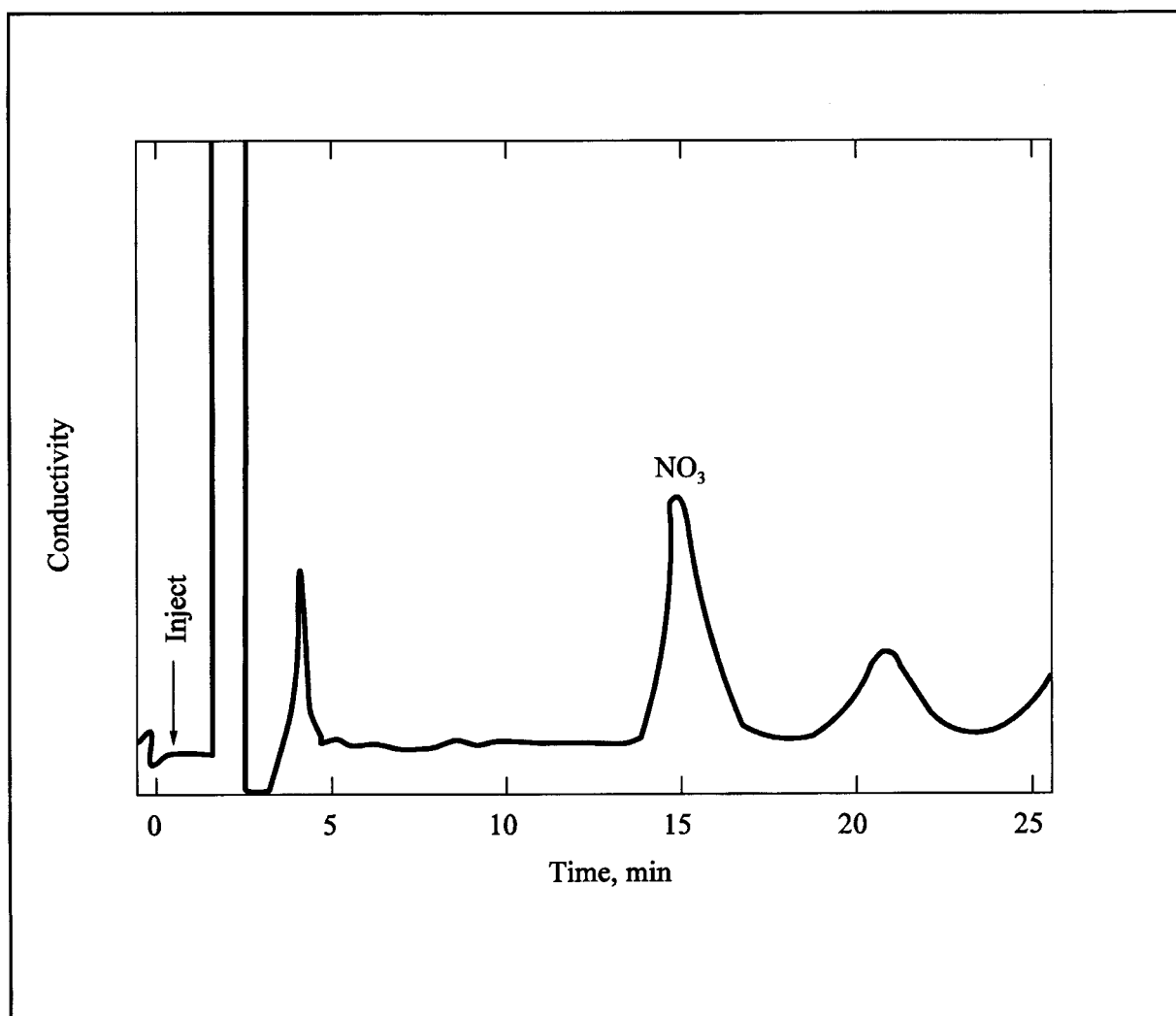


Figure 7D-1. Ion Chromatograph of a Prepared Sample.

BILLING CODE 6560-50-C

\* \* \* \* \*

### Method 8—Determination of Sulfuric Acid and Sulfur Dioxide Emissions From Stationary Sources

**Note:** This method does not include all of the specifications (*e.g.*, equipment and

supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge

of at least the following additional test

methods: Method 1, Method 2, Method 3, Method 5, and Method 6.

## 1.0 Scope and Application

### 1.1 Analytes.

Analyte	CAS No.	Sensitivity
Sulfuric acid, including: Sulfuric acid (H <sub>2</sub> SO <sub>4</sub> ) mist, Sulfur trioxide (SO <sub>3</sub> ).	7664-93-9, 7449-11-9 .....	0.05 mg/m <sup>3</sup> (0.03 × 10 <sup>-7</sup> lb/ft <sup>3</sup> ).
Sulfur dioxide (SO <sub>2</sub> ) .....	7449-09-5 .....	1.2 mg/m <sup>3</sup> (3 × 10 <sup>-9</sup> lb/ft <sup>3</sup> ).

1.2 Applicability. This method is applicable for the determination of H<sub>2</sub>SO<sub>4</sub> (including H<sub>2</sub>SO<sub>4</sub> mist and SO<sub>3</sub>) and gaseous SO<sub>2</sub> emissions from stationary sources.

**Note:** Filterable particulate matter may be determined along with H<sub>2</sub>SO<sub>4</sub> and SO<sub>2</sub> (subject to the approval of the Administrator) by inserting a heated glass fiber filter between the probe and isopropanol impinger (see Section 6.1.1 of Method 6). If this option is chosen, particulate analysis is gravimetric only; sulfuric acid is not determined separately.

### 1.3 Data Quality Objectives.

Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

## 2.0 Summary of Method

A gas sample is extracted isokinetically from the stack. The H<sub>2</sub>SO<sub>4</sub> and the SO<sub>2</sub> are separated, and both fractions are measured separately by the barium-thorin titration method.

## 3.0 Definitions. [Reserved]

## 4.0 Interferences

4.1 Possible interfering agents of this method are fluorides, free ammonia, and dimethyl aniline. If any of these interfering agents is present (this can be determined by knowledge of the process), alternative methods, subject to the approval of the Administrator, are required.

## 5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. Same as Method 6, Section 5.2.

## 6.0 Equipment and Supplies

6.1 Sample Collection. Same as Method 5, Section 6.1, with the following additions and exceptions:

6.1.1 Sampling Train. A schematic of the sampling train used in this

method is shown in Figure 8-1; it is similar to the Method 5 sampling train, except that the filter position is different, and the filter holder does not have to be heated. See Method 5, Section 6.1.1, for details and guidelines on operation and maintenance.

6.1.1.1 Probe Liner. Borosilicate or quartz glass, with a heating system to prevent visible condensation during sampling. Do not use metal probe liners.

6.1.1.2 Filter Holder. Borosilicate glass, with a glass frit filter support and a silicone rubber gasket. Other gasket materials (e.g., Teflon or Viton) may be used, subject to the approval of the Administrator. The holder design shall provide a positive seal against leakage from the outside or around the filter. The filter holder shall be placed between the first and second impingers. Do not heat the filter holder.

6.1.1.3 Impingers. Four, of the Greenburg-Smith design, as shown in Figure 8-1. The first and third impingers must have standard tips. The second and fourth impingers must be modified by replacing the insert with an approximately 13-mm (½-in.) ID glass tube, having an unobstructed tip located 13 mm (½ in.) from the bottom of the impinger. Similar collection systems, subject to the approval of the Administrator, may be used.

6.1.1.4 Temperature Sensor. Thermometer, or equivalent, to measure the temperature of the gas leaving the impinger train to within 1 °C (2 °F).

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Wash Bottles. Two polyethylene or glass bottles, 500-ml.

6.2.2 Graduated Cylinders. Two graduated cylinders (volumetric flasks may be used), 250-ml, 1-liter.

6.2.3 Storage Bottles. Leak-free polyethylene bottles, 1-liter size (two for each sampling run).

6.2.4 Trip Balance. 500-g capacity, to measure to ± 0.5 g (necessary only if a moisture content analysis is to be done).

6.3 Analysis. The following items are required for sample analysis:

6.3.1 Pipettes. Volumetric 10-ml, 100-ml.

6.3.2 Burette. 50-ml.

6.3.3 Erlenmeyer Flask. 250-ml (one for each sample, blank, and standard).

6.3.4 Graduated Cylinder. 100-ml.

6.3.5 Dropping Bottle. To add indicator solution, 125-ml size.

## 7.0 Reagents and Standards

**Note:** Unless otherwise indicated, all reagents are to conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Filters and Silica Gel. Same as in Method 5, Sections 7.1.1 and 7.1.2, respectively.

7.1.2 Water. Same as in Method 6, Section 7.1.1.

7.1.3 Isopropanol, 80 Percent by Volume. Mix 800 ml of isopropanol with 200 ml of water.

**Note:** Check for peroxide impurities using the procedure outlined in Method 6, Section 7.1.2.1.

7.1.4 Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>), 3 Percent by Volume. Dilute 100 ml of 30 percent H<sub>2</sub>O<sub>2</sub> to 1 liter with water. Prepare fresh daily.

7.1.5 Crushed Ice.

7.2 Sample Recovery. The reagents and standards required for sample recovery are:

7.2.1 Water. Same as in Section 7.1.2.

7.2.2 Isopropanol, 80 Percent. Same as in Section 7.1.3.

7.3 Sample Analysis. Same as Method 6, Section 7.3.

7.3.1 Quality Assurance Audit Samples. When making compliance determinations, and upon availability, audit samples may be obtained from the appropriate EPA Regional Office or from the responsible enforcement authority.

**Note:** The responsible enforcement authority should be notified at least 30 days prior to the test date to allow sufficient time for sample delivery.

## 8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Preparation. Same as Method 5, Section 8.1, except that filters should be inspected but need not be desiccated, weighed, or identified. If the

effluent gas can be considered dry (i.e., moisture-free), the silica gel need not be weighed.

#### 8.2 Preliminary Determinations.

Same as Method 5, Section 8.2.

#### 8.3 Preparation of Sampling Train.

Same as Method 5, Section 8.3, with the following exceptions:

8.3.1 Use Figure 8-1 instead of Figure 5-1.

8.3.2 Replace the second sentence of Method 5, Section 8.3.1 with: Place 100 ml of 80 percent isopropanol in the first impinger, 100 ml of 3 percent H<sub>2</sub>O<sub>2</sub> in both the second and third impingers; retain a portion of each reagent for use as a blank solution. Place about 200 g of silica gel in the fourth impinger.

8.3.3 Ignore any other statements in Section 8.3 of Method 5 that are obviously not applicable to the performance of Method 8.

**Note:** If moisture content is to be determined by impinger analysis, weigh each of the first three impingers (plus absorbing solution) to the nearest 0.5 g, and record these weights. Weigh also the silica gel (or silica gel plus container) to the nearest 0.5 g, and record.)

8.4 Metering System Leak-Check Procedure. Same as Method 5, Section 8.4.1.

8.5 Pretest Leak-Check Procedure. Follow the basic procedure in Method 5, Section 8.4.2, noting that the probe heater shall be adjusted to the minimum temperature required to prevent condensation, and also that verbage such as “\* \* \* plugging the inlet to the filter holder \* \* \*” found in Section 8.4.2.2 of Method 5 shall be replaced by “\* \* \* plugging the inlet to the first impinger \* \* \*”. The pretest leak-check is recommended, but is not required.

8.6 Sampling Train Operation. Follow the basic procedures in Method 5, Section 8.5, in conjunction with the following special instructions:

8.6.1 Record the data on a sheet similar to that shown in Figure 8-2 (alternatively, Figure 5-2 in Method 5 may be used). The sampling rate shall not exceed 0.030 m<sup>3</sup>/min (1.0 cfm) during the run. Periodically during the

test, observe the connecting line between the probe and first impinger for signs of condensation. If condensation does occur, adjust the probe heater setting upward to the minimum temperature required to prevent condensation. If component changes become necessary during a run, a leak-check shall be performed immediately before each change, according to the procedure outlined in Section 8.4.3 of Method 5 (with appropriate modifications, as mentioned in Section 8.5 of this method); record all leak rates. If the leakage rate(s) exceeds the specified rate, the tester shall either void the run or plan to correct the sample volume as outlined in Section 12.3 of Method 5. Leak-checks immediately after component changes are recommended, but not required. If these leak-checks are performed, the procedure in Section 8.4.2 of Method 5 (with appropriate modifications) shall be used.

8.6.2 After turning off the pump and recording the final readings at the conclusion of each run, remove the probe from the stack. Conduct a post-test (mandatory) leak-check as outlined in Section 8.4.4 of Method 5 (with appropriate modifications), and record the leak rate. If the post-test leakage rate exceeds the specified acceptable rate, either correct the sample volume, as outlined in Section 12.3 of Method 5, or void the run.

8.6.3 Drain the ice bath and, with the probe disconnected, purge the remaining part of the train by drawing clean ambient air through the system for 15 minutes at the average flow rate used for sampling.

**Note:** Clean ambient air can be provided by passing air through a charcoal filter. Alternatively, ambient air (without cleaning) may be used.

8.7 Calculation of Percent Isokinetic. Same as Method 5, Section 8.6.

8.8 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the

probe to cool. Treat the samples as follows:

#### 8.8.1 Container No. 1.

8.8.1.1 If a moisture content analysis is to be performed, clean and weigh the first impinger (plus contents) to the nearest 0.5 g, and record this weight.

8.8.1.2 Transfer the contents of the first impinger to a 250-ml graduated cylinder. Rinse the probe, first impinger, all connecting glassware before the filter, and the front half of the filter holder with 80 percent isopropanol. Add the isopropanol rinse solution to the cylinder. Dilute the contents of the cylinder to 225 ml with 80 percent isopropanol, and transfer the cylinder contents to the storage container. Rinse the cylinder with 25 ml of 80 percent isopropanol, and transfer the rinse to the storage container. Add the filter to the solution in the storage container and mix. Seal the container to protect the solution against evaporation. Mark the level of liquid on the container, and identify the sample container.

#### 8.8.2 Container No. 2.

8.8.2.1 If a moisture content analysis is to be performed, clean and weigh the second and third impingers (plus contents) to the nearest 0.5 g, and record the weights. Also, weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g, and record the weight.

8.8.2.2 Transfer the solutions from the second and third impingers to a 1-liter graduated cylinder. Rinse all connecting glassware (including back half of filter holder) between the filter and silica gel impinger with water, and add this rinse water to the cylinder. Dilute the contents of the cylinder to 950 ml with water. Transfer the solution to a storage container. Rinse the cylinder with 50 ml of water, and transfer the rinse to the storage container. Mark the level of liquid on the container. Seal and identify the sample container.

### 9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
7.1.3 .....	Isopropanol check .....	Ensure acceptable level of peroxide impurities in isopropanol.
8.4, 8.5, 10.1 .....	Sampling equipment leak-check and calibration.	Ensure accurate measurement of stack gas flow rate, sample volume.
10.2 .....	Barium standard solution standardization .....	Ensure normality determination.
11.2 .....	Replicate titrations .....	Ensure precision of titration determinations.
11.3 .....	Audit sample analysis .....	Evaluate analyst's technique and standards preparation.

9.2 Volume Metering System Checks. Same as Method 5, Section 9.2.

### 10.0 Calibration and Standardization

10.1 Sampling Equipment. Same as Method 5, Section 10.0.

10.2 Barium Standard Solution. Same as Method 6, Section 10.5.

### 11.0 Analytical Procedure

11.1. Sample Loss. Same as Method 6, Section 11.1.

11.2. Sample Analysis.

11.2.1 Container No. 1. Shake the container holding the isopropanol solution and the filter. If the filter breaks up, allow the fragments to settle for a few minutes before removing a sample aliquot. Pipette a 100-ml aliquot of this solution into a 250-ml Erlenmeyer flask, add 2 to 4 drops of thorin indicator, and titrate to a pink endpoint using 0.0100 N barium standard solution. Repeat the titration with a second aliquot of sample, and average the titration values. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is greater.

11.2.2 Container No. 2. Thoroughly mix the solution in the container holding the contents of the second and third impingers. Pipette a 10-ml aliquot of sample into a 250-ml Erlenmeyer flask. Add 40 ml of isopropanol, 2 to 4 drops of thorin indicator, and titrate to a pink endpoint using 0.0100 N barium standard solution. Repeat the titration with a second aliquot of sample, and average the titration values. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is greater.

11.2.3 Blanks. Prepare blanks by adding 2 to 4 drops of thorin indicator to 100 ml of 80 percent isopropanol. Titrate the blanks in the same manner as the samples.

11.3 Audit Sample Analysis.

11.3.1 When the method is used to analyze samples to demonstrate compliance with a source emission regulation, EPA audit samples must be analyzed, subject to availability.

11.3.2 Concurrently analyze audit samples and the compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation.

**Note:** It is recommended that known quality control samples be analyzed prior to the compliance and audit sample analyses to optimize the system accuracy and precision. These quality control samples may be obtained by contacting the appropriate EPA regional Office or the responsible enforcement authority.

11.3.3 The same analyst, analytical reagents, and analytical system shall be used for the compliance samples and the EPA audit samples. If this condition is met, duplicate auditing of subsequent compliance analyses for the same enforcement agency within a 30-day period is waived. Audit samples may not be used to validate different compliance samples under the jurisdiction of separate enforcement agencies, unless prior arrangements have been made with both enforcement agencies.

11.4 Audit Sample Results.

11.4.1 Calculate the audit sample concentrations in mg/dscm and submit results using the instructions provided with the audit samples.

11.4.2 Report the results of the audit samples and the compliance determination samples along with their identification numbers, and the analyst's name to the responsible enforcement authority. Include this information with reports of any subsequent compliance analyses for the same enforcement authority during the 30-day period.

11.4.3 The concentrations of the audit samples obtained by the analyst shall agree within 5 percent of the actual concentrations. If the 5 percent specification is not met, reanalyze the compliance and audit samples, and include initial and reanalysis values in the test report.

11.4.4 Failure to meet the 5 percent specification may require retests until the audit problems are resolved. However, if the audit results do not affect the compliance or noncompliance status of the affected facility, the Administrator may waive the reanalysis requirement, further audits, or retests and accept the results of the compliance test. While steps are being taken to resolve audit analysis problems, the Administrator may also choose to use the data to determine the compliance or noncompliance status of the affected facility.

### 12.0 Data Analysis and Calculations

Carry out calculations retaining at least one extra significant figure beyond

that of the acquired data. Round off figures after final calculation.

12.1 Nomenclature. Same as Method 5, Section 12.1, with the following additions and exceptions:

$C_a$  = Actual concentration of SO<sub>2</sub> in audit sample, mg/dscm.

$C_d$  = Determined concentration of SO<sub>2</sub> in audit sample, mg/dscm.

$C_{H_2SO_4}$  = Sulfuric acid (including SO<sub>3</sub>) concentration, g/dscm (lb/dscf).

$C_{SO_2}$  = Sulfur dioxide concentration, g/dscm (lb/dscf).

$N$  = Normality of barium perchlorate titrant, meq/ml.

$RE$  = Relative error of QA audit sample analysis, percent

$V_a$  = Volume of sample aliquot titrated, 100 ml for H<sub>2</sub>SO<sub>4</sub> and 10 ml for SO<sub>2</sub>.

$V_{soln}$  = Total volume of solution in which the sample is contained, 250 ml for the SO<sub>2</sub> sample and 1000 ml for the H<sub>2</sub>SO<sub>4</sub> sample.

$V_t$  = Volume of barium standard solution titrant used for the sample, ml.

$V_{tb}$  = Volume of barium standard solution titrant used for the blank, ml.

12.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop. See data sheet (Figure 8-2).

12.3 Dry Gas Volume. Same as Method 5, Section 12.3.

12.4 Volume of Water Vapor Condensed and Moisture Content. Calculate the volume of water vapor using Equation 5-2 of Method 5; the weight of water collected in the impingers and silica gel can be converted directly to milliliters (the specific gravity of water is 1 g/ml). Calculate the moisture content of the stack gas ( $B_{ws}$ ) using Equation 5-3 of Method 5. The **Note** in Section 12.5 of Method 5 also applies to this method. Note that if the effluent gas stream can be considered dry, the volume of water vapor and moisture content need not be calculated.

12.5 Sulfuric Acid Mist (Including SO<sub>3</sub>) Concentration.

$$C_{H_2SO_4} = K_3 \left[ N (V_t - V_{tb}) (V_{soln} / V_a) \right] / V_{m(std)} \quad \text{Eq. 8-1}$$

Where:

$K_3$  = 0.04904 g/meq for metric units,

$K_3$  =  $1.081 \times 10^{-4}$  lb/meq for English units.

### 12.6 Sulfur Dioxide Concentration.

$$C_{SO_2} = K_4 \left[ N (V_t - V_{tb}) (V_{soln} / V_a) \right] / V_{m(std)} \quad \text{Eq. 8-2}$$



Where:

$K_4 = 0.03203$  g/meq for metric units,  
 $K_4 = 7.061 \times 10^{-5}$  lb/meq for English  
units.

12.7 Isokinetic Variation. Same as  
Method 5, Section 12.11.

12.8 Stack Gas Velocity and  
Volumetric Flow Rate. Calculate the  
average stack gas velocity and  
volumetric flow rate, if needed, using  
data obtained in this method and the  
equations in Sections 12.6 and 12.7 of  
Method 2.

12.9 Relative Error (RE) for QA  
Audit Samples. Same as Method 6,  
Section 12.4.

### 13.0 Method Performance

13.1 Analytical Range. Collaborative  
tests have shown that the minimum  
detectable limits of the method are  $0.06$   
 $\text{mg/m}^3$  ( $4 \times 10^{-9}$  lb/ft<sup>3</sup>) for H<sub>2</sub>SO<sub>4</sub> and  
 $1.2$  mg/m<sup>3</sup> ( $74 \times 10^{-9}$  lb/ft<sup>3</sup>) for SO<sub>2</sub>. No  
upper limits have been established.  
Based on theoretical calculations for 200  
ml of 3 percent H<sub>2</sub>O<sub>2</sub> solution, the upper  
concentration limit for SO<sub>2</sub> in a 1.0 m<sup>3</sup>

(35.3 ft<sup>3</sup>) gas sample is about 12,000 mg/  
m<sup>3</sup> ( $7.7 \times 10^{-4}$  lb/ft<sup>3</sup>). The upper limit  
can be extended by increasing the  
quantity of peroxide solution in the  
impingers.

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

### 16.0 References

Same as Section 17.0 of Methods 5  
and 6.

BILLING CODE 6560-50-C

## 17.0 Tables, Diagrams, Flowcharts, and Validation Data

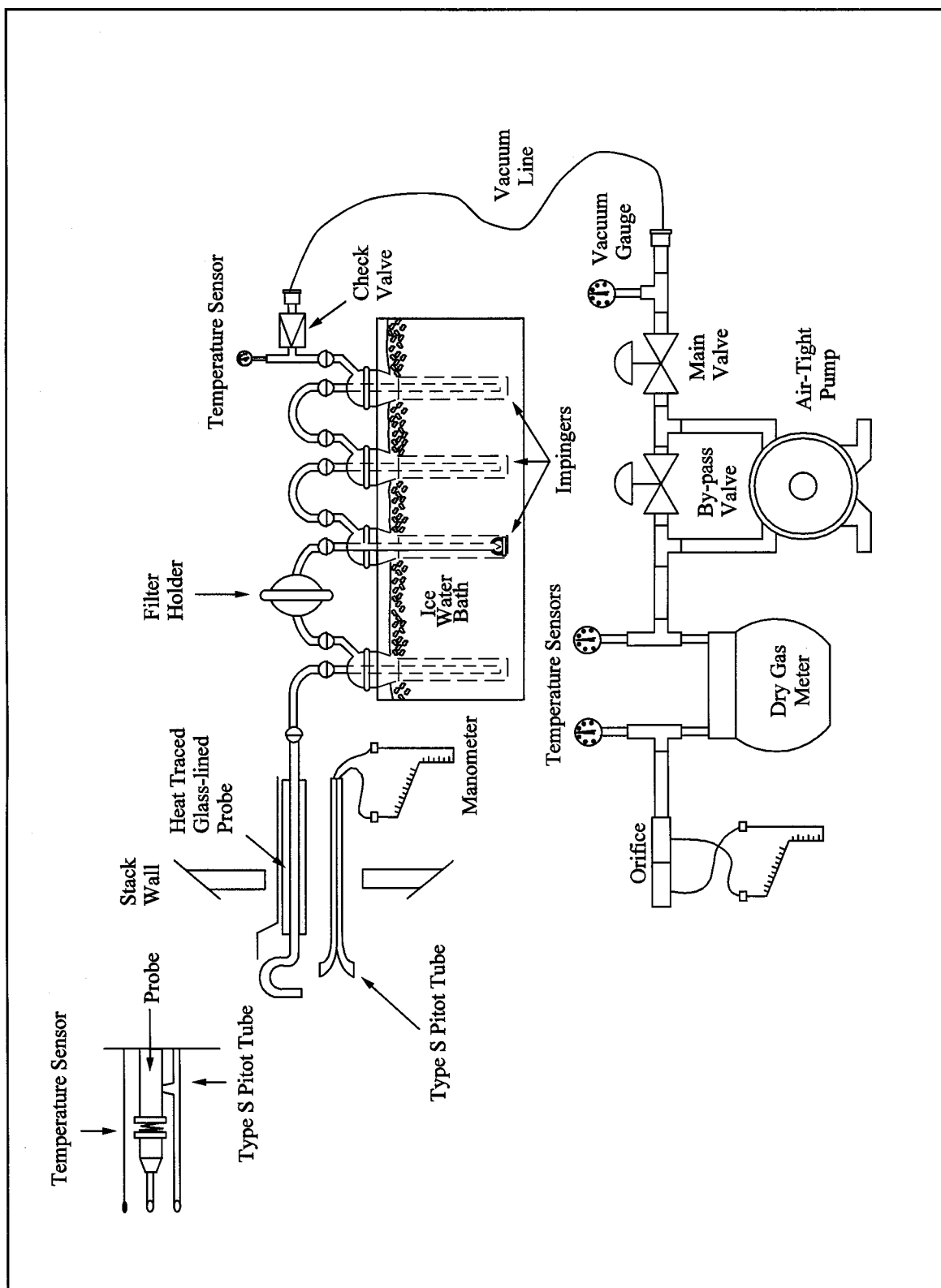


Figure 8-1. Sulfuric Acid Sampling Train.

Plant \_\_\_\_\_

Location \_\_\_\_\_

Operator \_\_\_\_\_

Date \_\_\_\_\_

Run No. \_\_\_\_\_

Sample box No. \_\_\_\_\_

Meter box No. \_\_\_\_\_

Meter  $\Delta H @$  \_\_\_\_\_

C factor \_\_\_\_\_

Pitot tube coefficient,  $C_p$  \_\_\_\_\_

Ambient temperature \_\_\_\_\_

Barometric pressure \_\_\_\_\_

Assumed moisture, % \_\_\_\_\_

Probe length, (ft.) \_\_\_\_\_

Nozzle identification No. \_\_\_\_\_

Average calibrated nozzle diameter, (in.) \_\_\_\_\_

Probe heater setting \_\_\_\_\_

Leak rate, (cfm) \_\_\_\_\_

Static pressure, (in. Hg) \_\_\_\_\_

Probe liner material \_\_\_\_\_

Filter No. \_\_\_\_\_

SCHEMATIC OF STACK  
CROSS SECTION

Traverse point number	Sampling time min.	Vacuum (in.Hg)	Stack temperature ( $T_s$ ) (°F)	Velocity head ( $\Delta P_s$ ) (in. $H_2O$ )	Pressure differential across orifice meter (in. $H_2O$ )	Gas meter reading (ft³)	Gas sample temperature at dry gas meter		Filter temperature (°F)	Temperature of gas leaving condenser or last impinger (°F)
							Inlet (°F)	Outlet (°F)		
Total							Avg.	Avg.		
Average							Avg.	Avg.		

\* \* \* \* \*

# Method 10A—Determination of Carbon Monoxide Emissions in Certifying Continuous Emission Monitoring Systems at Petroleum Refineries

**Note:** This method does not include all of the specifications (e.g., equipment and

supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test

methods: Method 1, Method 4, and Method 5.

## 1.0 Scope and Application

### 1.1 Analytes.

Analyte	CAS No.	Sensitivity
Carbon monoxide (CO) .....	630-08-0	3 ppmv

1.2 Applicability. This method is applicable for the determination of CO emissions at petroleum refineries. This method serves as the reference method in the relative accuracy test for nondispersive infrared (NDIR) CO continuous emission monitoring systems (CEMS) that are required to be installed in petroleum refineries on fluid catalytic cracking unit catalyst regenerators (§ 60.105(a)(2) of this part).

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

## 2.0 Summary of Method

An integrated gas sample is extracted from the stack, passed through an alkaline permanganate solution to remove sulfur oxides and nitrogen oxides, and collected in a Tedlar bag. The CO concentration in the sample is measured spectrophotometrically using the reaction of CO with *p*-sulfaminobenzoic acid.

## 3.0 Definitions. [Reserved]

## 4.0 Interferences

Sulfur oxides, nitric oxide, and other acid gases interfere with the colorimetric reaction. They are removed by passing the sampled gas through an alkaline potassium permanganate scrubbing solution. Carbon dioxide (CO<sub>2</sub>) does not interfere, but, because it is removed by the scrubbing solution, its concentration must be measured independently and an appropriate volume correction made to the sampled gas.

## 5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions to be

taken with regard to the analytical procedure.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

## 6.0 Equipment and Supplies

6.1 Sample Collection. The sampling train shown in Figure 10A-1 is required for sample collection. Component parts are described below:

6.1.1 Probe. Stainless steel, sheathed Pyrex glass, or equivalent, equipped with a glass wool plug to remove particulate matter.

6.1.2 Sample Conditioning System. Three Greenburg-Smith impingers connected in series with leak-free connections.

6.1.3 Pump. Leak-free pump with stainless steel and Teflon parts to transport sample at a flow rate of 300 ml/min (0.01 ft<sup>3</sup>/min) to the flexible bag.

6.1.4 Surge Tank. Installed between the pump and the rate meter to eliminate the pulsation effect of the pump on the rate meter.

6.1.5 Rate Meter. Rotameter, or equivalent, to measure flow rate at 300 ml/min (0.01 ft<sup>3</sup>/min). Calibrate according to Section 10.2.

6.1.6 Flexible Bag. Tedlar, or equivalent, with a capacity of 10 liters (0.35 ft<sup>3</sup>) and equipped with a sealing quick-connect plug. The bag must be leak-free according to Section 8.1. For protection, it is recommended that the bag be enclosed within a rigid container.

6.1.7 Valves. Stainless-steel needle valve to adjust flow rate, and stainless-steel three-way valve, or equivalent.

6.1.8 CO<sub>2</sub> Analyzer. Fyrite, or equivalent, to measure CO<sub>2</sub> concentration to within 0.5 percent.

6.1.9 Volume Meter. Dry gas meter, capable of measuring the sample volume under calibration conditions of 300 ml/min (0.01 ft<sup>3</sup>/min) for 10 minutes.

6.1.10 Pressure Gauge. A water filled U-tube manometer, or equivalent, of about 30 cm (12 in.) to leak-check the flexible bag.

## 6.2 Sample Analysis.

6.2.1 Spectrophotometer. Single- or double-beam to measure absorbance at 425 and 600 nm. Slit width should not exceed 20 nm.

6.2.2 Spectrophotometer Cells. 1-cm pathlength.

6.2.3 Vacuum Gauge. U-tube mercury manometer, 1 meter (39 in.), with 1-mm divisions, or other gauge capable of measuring pressure to within 1 mm Hg.

6.2.4 Pump. Capable of evacuating the gas reaction bulb to a pressure equal to or less than 40 mm Hg absolute, equipped with coarse and fine flow control valves.

6.2.5 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 1 mm Hg.

6.2.6 Reaction Bulbs. Pyrex glass, 100-ml with Teflon stopcock (Figure 10A-2), leak-free at 40 mm Hg, designed so that 10 ml of the colorimetric reagent can be added and removed easily and accurately. Commercially available gas sample bulbs such as Supelco Catalog No. 2-2161 may also be used.

6.2.7 Manifold. Stainless steel, with connections for three reaction bulbs and the appropriate connections for the manometer and sampling bag as shown in Figure 10A-3.

6.2.8 Pipets. Class A, 10-ml size.

6.2.9 Shaker Table. Reciprocating-stroke type such as Eberbach Corporation, Model 6015. A rocking arm or rotary-motion type shaker may also be used. The shaker must be large enough to accommodate at least six gas sample bulbs simultaneously. It may be necessary to construct a table top extension for most commercial shakers to provide sufficient space for the needed bulbs (Figure 10A-4).

6.2.10 Valve. Stainless steel shut-off valve.

6.2.11 Analytical Balance. Capable of weighing to 0.1 mg.

## 7.0 Reagents and Standards

Unless otherwise indicated, all reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, the best available grade shall be used.

### 7.1 Sample Collection.

7.1.1 Water. Deionized distilled, to conform to ASTM D 1193-77 or 91, Type 3 (incorporated by reference—see § 60.17). If high concentrations of organic matter are not expected to be present, the potassium permanganate test for oxidizable organic matter may be omitted.

7.1.2 Alkaline Permanganate Solution, 0.25 M  $\text{KMnO}_4$ /1.5 M Sodium Hydroxide (NaOH). Dissolve 40 g  $\text{KMnO}_4$  and 60 g NaOH in approximately 900 ml water, cool, and dilute to 1 liter.

### 7.2 Sample Analysis.

7.2.1 Water. Same as in Section 7.1.1.

7.2.2 1 M Sodium Hydroxide Solution. Dissolve 40 g NaOH in approximately 900 ml of water, cool, and dilute to 1 liter.

7.2.3 0.1 M NaOH Solution. Dilute 50 ml of the 1 M NaOH solution prepared in Section 7.2.2 to 500 ml.

7.2.4 0.1 M Silver Nitrate ( $\text{AgNO}_3$ ) Solution. Dissolve 8.5 g  $\text{AgNO}_3$  in water, and dilute to 500 ml.

7.2.5 0.1 M Para-Sulfaminobenzoic Acid (p-SABA) Solution. Dissolve 10.0 g p-SABA in 0.1 M NaOH, and dilute to 500 ml with 0.1 M NaOH.

7.2.6 Colorimetric Solution. To a flask, add 100 ml of 0.1 M p-SABA solution and 100 ml of 0.1 M  $\text{AgNO}_3$  solution. Mix, and add 50 ml of 1 M

NaOH with shaking. The resultant solution should be clear and colorless. This solution is acceptable for use for a period of 2 days.

7.2.7 Standard Gas Mixtures. Traceable to National Institute of Standards and Technology (NIST) standards and containing between 50 and 1000 ppm CO in nitrogen. At least two concentrations are needed to span each calibration range used (Section 10.3). The calibration gases must be certified by the manufacturer to be within 2 percent of the specified concentrations.

## 8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sample Bag Leak-Checks. While a bag leak-check is required after bag use, it should also be done before the bag is used for sample collection. The bag should be leak-checked in the inflated and deflated condition according to the following procedure:

8.1.1 Connect the bag to a water manometer, and pressurize the bag to 5 to 10 cm  $\text{H}_2\text{O}$  (2 to 4 in  $\text{H}_2\text{O}$ ). Allow the bag to stand for 60 minutes. Any displacement in the water manometer indicates a leak.

8.1.2 Evacuate the bag with a leakless pump that is connected to the downstream side of a flow indicating device such as a 0- to 100-ml/min rotameter or an impinger containing water. When the bag is completely evacuated, no flow should be evident if the bag is leak-free.

### 8.2 Sample Collection.

8.2.1 Evacuate the Tedlar bag completely using a vacuum pump. Assemble the apparatus as shown in Figure 10A-1. Loosely pack glass wool in the tip of the probe. Place 400 ml of alkaline permanganate solution in the

first two impingers and 250 ml in the third. Connect the pump to the third impinger, and follow this with the surge tank, rate meter, and 3-way valve. Do not connect the Tedlar bag to the system at this time.

8.2.2 Leak-check the sampling system by plugging the probe inlet, opening the 3-way valve, and pulling a vacuum of approximately 250 mm Hg on the system while observing the rate meter for flow. If flow is indicated on the rate meter, do not proceed further until the leak is found and corrected.

8.2.3 Purge the system with sample gas by inserting the probe into the stack and drawing the sample gas through the system at 300 ml/min  $\pm$  10 percent for 5 minutes. Connect the evacuated Tedlar bag to the system, record the starting time, and sample at a rate of 300 ml/min for 30 minutes, or until the Tedlar bag is nearly full. Record the sampling time, the barometric pressure, and the ambient temperature. Purge the system as described above immediately before each sample.

8.2.4 The scrubbing solution is adequate for removing sulfur oxides and nitrogen oxides from 50 liters (1.8 ft<sup>3</sup>) of stack gas when the concentration of each is less than 1,000 ppm and the  $\text{CO}_2$  concentration is less than 15 percent. Replace the scrubber solution after every fifth sample.

8.3 Carbon Dioxide Measurement. Measure the  $\text{CO}_2$  content in the stack to the nearest 0.5 percent each time a CO sample is collected. A simultaneous grab sample analyzed by the Fyrite analyzer is acceptable.

## 9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.1 .....	Sampling equipment leak-checks and calibration.	Ensure accuracy and precision of sampling measurements.
10.3 .....	Spectrophotometer calibration .....	Ensure linearity of spectrophotometer response to standards.

9.2 Volume Metering System Checks. Same as Method 5, Section 9.2.

## 10.0 Calibration and Standardization

**Note:** Maintain a laboratory log of all calibrations.

10.1 Gas Bulb Calibration. Weigh the empty bulb to the nearest 0.1 g. Fill the bulb to the stopcock with water, and again weigh to the nearest 0.1 g. Subtract the tare weight, and calculate the volume in liters to three significant figures using the density of water at the measurement temperature. Record the

volume on the bulb. Alternatively, mark an identification number on the bulb, and record the volume in a notebook.

### 10.2 Rate Meter Calibration.

Assemble the system as shown in Figure 10A-1 (the impingers may be removed), and attach a volume meter to the probe inlet. Set the rotameter at 300 ml/min, record the volume meter reading, start the pump, and pull ambient air through the system for 10 minutes. Record the final volume meter reading. Repeat the procedure and average the results to

determine the volume of gas that passed through the system.

### 10.3 Spectrophotometer Calibration Curve.

10.3.1 Collect the standards as described in Section 8.2. Prepare at least two sets of three bulbs as standards to span the 0 to 400 or 400 to 1000 ppm range. If any samples span both concentration ranges, prepare a calibration curve for each range using separate reagent blanks. Prepare a set of three bulbs containing colorimetric reagent but no CO to serve as a reagent

blank. Analyze each standard and blank according to the sample analysis procedure of Section 11.0. Reject the standard set where any of the individual bulb absorbances differs from the set mean by more than 10 percent.

10.3.2 Calculate the average absorbance for each set (3 bulbs) of standards using Equation 10A-1 and Table 10A-1. Construct a graph of average absorbance for each standard against its corresponding concentration. Draw a smooth curve through the points. The curve should be linear over the two concentration ranges discussed in Section 13.3.

#### 11.0 Analytical Procedure

11.1 Assemble the system shown in Figure 10A-3, and record the information required in Table 10A-1 as it is obtained. Pipet 10.0 ml of the colorimetric reagent into each gas reaction bulb, and attach the bulbs to the system. Open the stopcocks to the reaction bulbs, but leave the valve to the Tedlar bag closed. Turn on the pump, fully open the coarse-adjust flow valve, and slowly open the fine-adjust valve until the pressure is reduced to at least 40 mm Hg. Now close the coarse adjust valve, and observe the manometer to be certain that the system is leak-free. Wait a minimum of 2 minutes. If the pressure has increased less than 1 mm Hg, proceed as described below. If a leak is present, find and correct it before proceeding further.

11.2 Record the vacuum pressure ( $P_v$ ) to the nearest 1 mm Hg, and close the reaction bulb stopcocks. Open the Tedlar bag valve, and allow the system to come to atmospheric pressure. Close the bag valve, open the pump coarse adjust valve, and evacuate the system again. Repeat this fill/evacuation procedure at least twice to flush the manifold completely. Close the pump coarse adjust valve, open the Tedlar bag valve, and let the system fill to atmospheric pressure. Open the stopcocks to the reaction bulbs, and let the entire system come to atmospheric pressure. Close the bulb stopcocks, remove the bulbs, record the room temperature and barometric pressure ( $P_{bar}$ , to nearest mm Hg), and place the bulbs on the shaker table with their main axis either parallel to or perpendicular to the plane of the table top. Purge the bulb-filling system with ambient air for several minutes between samples. Shake the samples for exactly 2 hours.

11.3 Immediately after shaking, measure the absorbance ( $A$ ) of each bulb sample at 425 nm if the concentration is less than or equal to 400 ppm CO or

at 600 nm if the concentration is above 400 ppm.

**Note:** This may be accomplished with multiple bulb sets by sequentially collecting sets and adding to the shaker at staggered intervals, followed by sequentially removing sets from the shaker for absorbance measurement after the two-hour designated intervals have elapsed.

11.4 Use a small portion of the sample to rinse a spectrophotometer cell several times before taking an aliquot for analysis. If one cell is used to analyze multiple samples, rinse the cell with deionized distilled water several times between samples. Prepare and analyze standards and a reagent blank as described in Section 10.3. Use water as the reference. Reject the analysis if the blank absorbance is greater than 0.1. All conditions should be the same for analysis of samples and standards. Measure the absorbances as soon as possible after shaking is completed.

11.5 Determine the CO concentration of each bag sample using the calibration curve for the appropriate concentration range as discussed in Section 10.3.

#### 12.0 Calculations and Data Analysis

Carry out calculations retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

##### 12.1 Nomenclature.

$A$  = Sample absorbance, uncorrected for the reagent blank.

$A_r$  = Absorbance of the reagent blank.

$A_s$  = Average sample absorbance per liter, units/liter.

$B_w$  = Moisture content in the bag sample.

$C$  = CO concentration in the stack gas, dry basis, ppm.

$C_b$  = CO concentration of the bag sample, dry basis, ppm.

$C_g$  = CO concentration from the calibration curve, ppm.

$F$  = Volume fraction of  $CO_2$  in the stack.

$n$  = Number of reaction bulbs used per bag sample.

$P_b$  = Barometric pressure, mm Hg.

$P_v$  = Residual pressure in the sample bulb after evacuation, mm Hg.

$P_w$  = Vapor pressure of  $H_2O$  in the bag (from Table 10A-2), mm Hg.

$V_b$  = Volume of the sample bulb, liters.

$V_r$  = Volume of reagent added to the sample bulb, 0.0100 liter.

12.2 Average Sample Absorbance per Liter. Calculate  $A_s$  for each gas bulb using Equation 10A-1, and record the value in Table 10A-1. Calculate the average  $A_s$  for each bag sample, and compare the three values to the average. If any single value differs by more than 10 percent from the average, reject this

value, and calculate a new average using the two remaining values.

$$A_s = \frac{(A - A_r)(P_b)}{(V_b - V_r)(P_b - P_v)} \quad \text{Eq. 10A-1}$$

**Note:**  $A$  and  $A_r$  must be at the same wavelength.

12.3 CO Concentration in the Bag. Calculate  $C_b$  using Equations 10A-2 and 10A-3. If condensate is visible in the Tedlar bag, calculate  $B_w$  using Table 10A-2 and the temperature and barometric pressure in the analysis room. If condensate is not visible, calculate  $B_w$  using the temperature and barometric pressure at the sampling site.

$$B_w = \frac{P_w}{P_b} \quad \text{Eq. 10A-2}$$

$$C_b = \frac{C_g}{(1 - B_w)} \quad \text{Eq. 10A-3}$$

#### 12.4 CO Concentration in the Stack.

$$C = C_b (1 - F) \quad \text{Eq. 10A-4}$$

#### 13.0 Method Performance

13.1 Precision. The estimated intralaboratory standard deviation of the method is 3 percent of the mean for gas samples analyzed in duplicate in the concentration range of 39 to 412 ppm. The interlaboratory precision has not been established.

13.2 Accuracy. The method contains no significant biases when compared to an NDIR analyzer calibrated with NIST standards.

13.3 Range. Approximately 3 to 1800 ppm CO. Samples having concentrations below 400 ppm are analyzed at 425 nm, and samples having concentrations above 400 ppm are analyzed at 600 nm.

13.4 Sensitivity. The detection limit is 3 ppmv based on a change in concentration equal to three times the standard deviation of the reagent blank solution.

13.5 Stability. The individual components of the colorimetric reagent are stable for at least 1 month. The colorimetric reagent must be used within 2 days after preparation to avoid excessive blank correction. The samples in the Tedlar bag should be stable for at least 1 week if the bags are leak-free.

#### 14.0 Pollution Prevention. [Reserved]

#### 15.0 Waste Management. [Reserved]

#### 16.0 References

1. Butler, F.E., J.E. Knoll, and M.R. Midgett. Development and Evaluation of Methods for Determining Carbon Monoxide Emissions.

U.S. Environmental Protection Agency, Research Triangle Park, N.C. June 1985. 33 pp.

2. Ferguson, B.B., R.E. Lester, and W.J. Mitchell. Field Evaluation of Carbon Monoxide and Hydrogen Sulfide Continuous Emission Monitors at an Oil Refinery. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA-600/4-82-054. August 1982. 100 pp.

3. Lambert, J.L., and R.E. Weins. Induced Colorimetric Method for Carbon Monoxide.

Analytical Chemistry. 46(7):929-930. June 1974.

4. Levaggi, D.A., and M. Feldstein. The Colorimetric Determination of Low Concentrations of Carbon Monoxide. Industrial Hygiene Journal. 25:64-66. January-February 1964.

5. Repp, M. Evaluation of Continuous Monitors For Carbon Monoxide in Stationary Sources. U.S. Environmental Protection Agency. Research Triangle Park, N.C. Publication No. EPA-600/2-77-063. March 1977. 155 pp.

6. Smith, F., D.E. Wagoner, and R.P. Donovan. Guidelines for Development of a Quality Assurance Program: Volume VIII—Determination of CO Emissions from Stationary Sources by NDIR Spectrometry. U.S. Environmental Protection Agency. Research Triangle Park, N.C. Publication No. EPA-650/4-74-005-h. February 1975. 96 pp.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 10A-1.—DATA RECORDING SHEET FOR SAMPLES ANALYZED IN TRIPPLICATE

Sample No./type	Room temp °C	Stack %CO <sub>2</sub>	Bulb No.	Bulb vol. liters	Reagent vol. in bulb, liter	Partial pressure of gas in bulb, mm Hg	P <sub>b</sub> , mm Hg	Shaking time, min	Abs versus water	A-A <sub>r</sub>	A <sub>s</sub>	Avg A <sub>s</sub>
blank												
Std. 1												
Std. 2												
Sample 1												
Sample 2												
Sample 3												

TABLE 10A-2.—MOISTURE CORRECTION

Temperature °C	Vapor pressure of H <sub>2</sub> O, mm Hg	Temperature °C	Vapor pressure of H <sub>2</sub> , mm Hg
4 .....	6.1	18	15.5
6 .....	7.0	20	17.5
8 .....	8.0	22	19.8
10 .....	9.2	24	22.4
12 .....	10.5	26	25.2
14 .....	12.0	28	28.3
16 .....	13.6	30	31.8

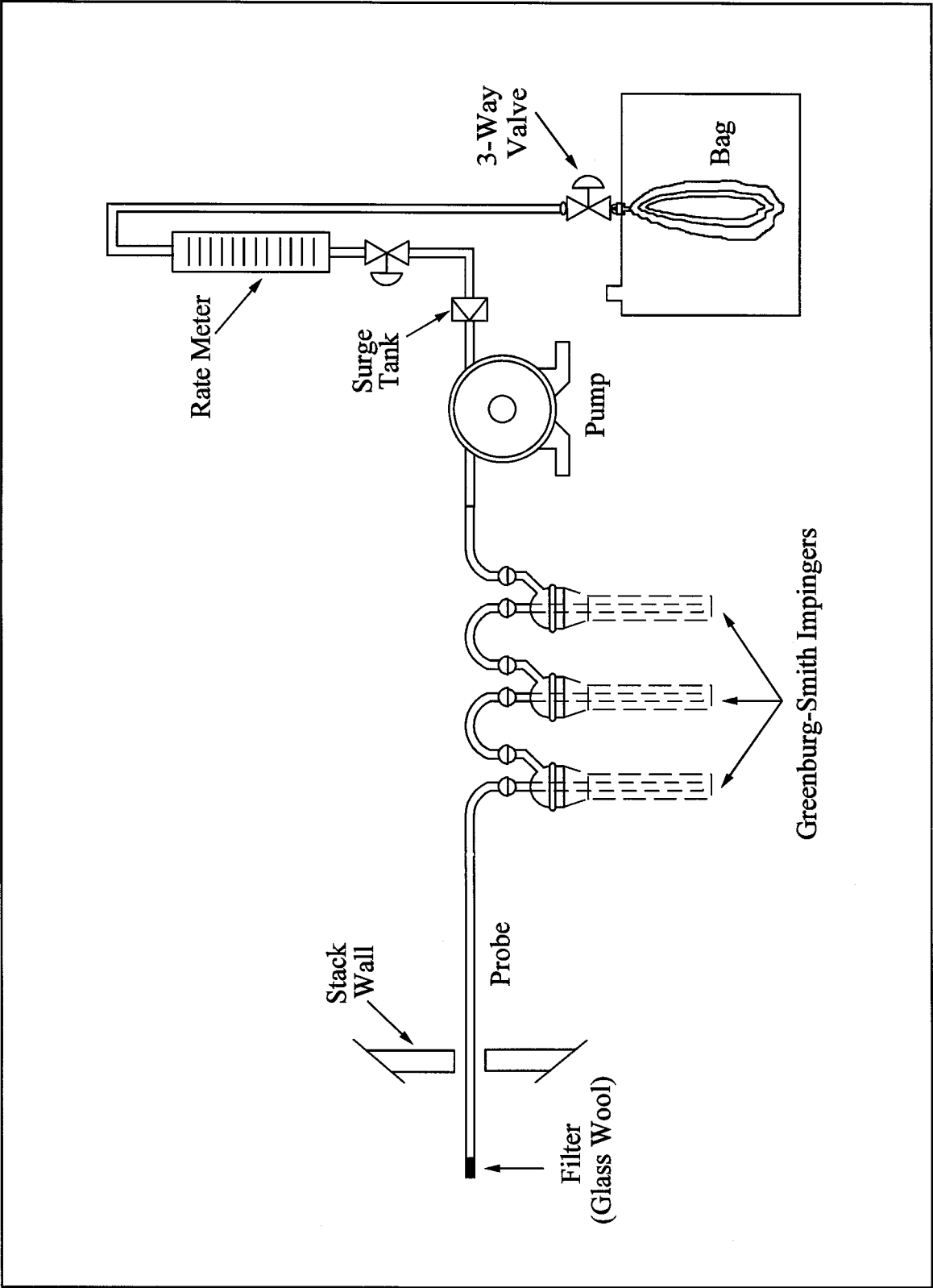


Figure 10A-1. Sampling Train.



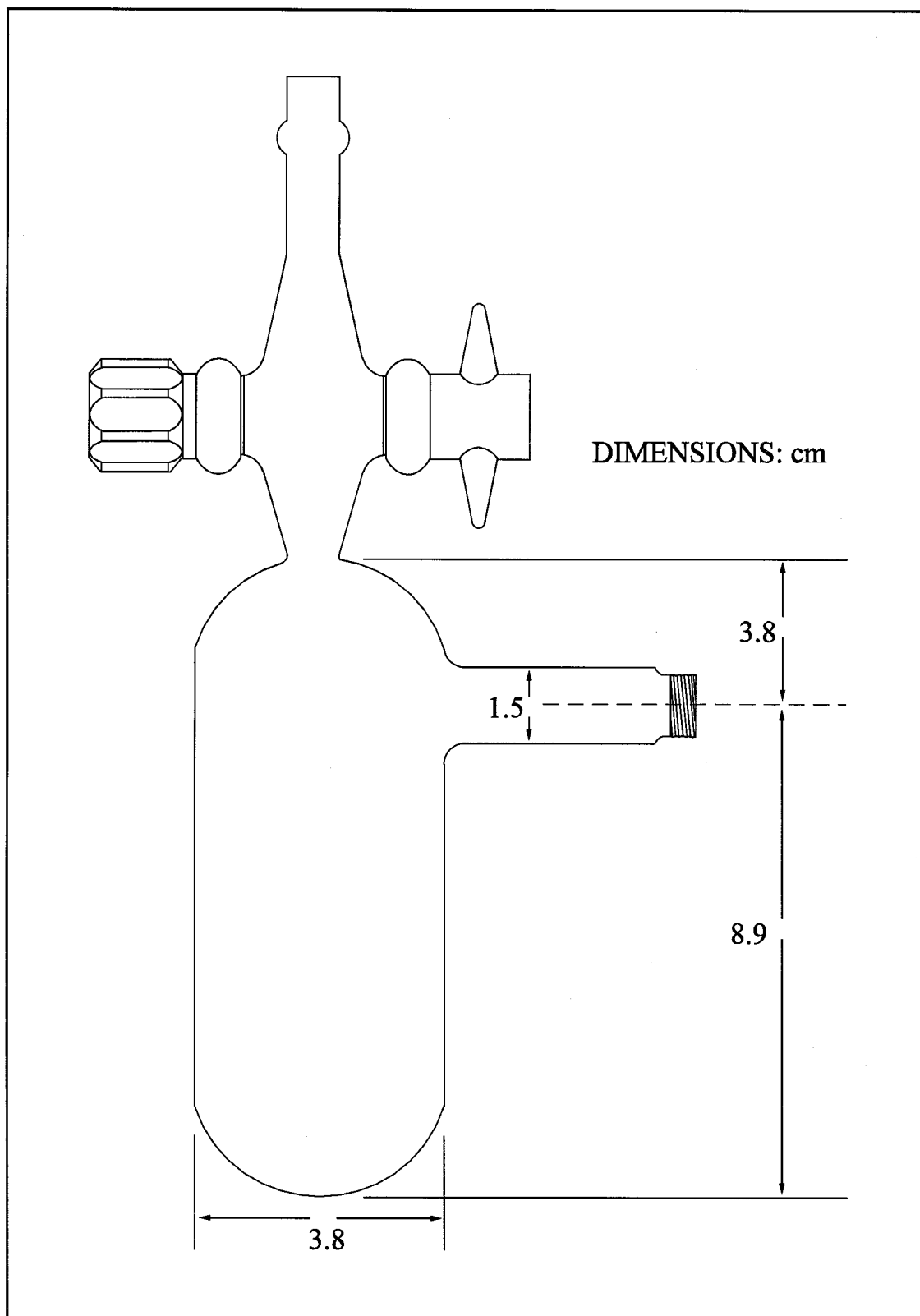


Figure 10A-2. Sample Reaction Bulbs.

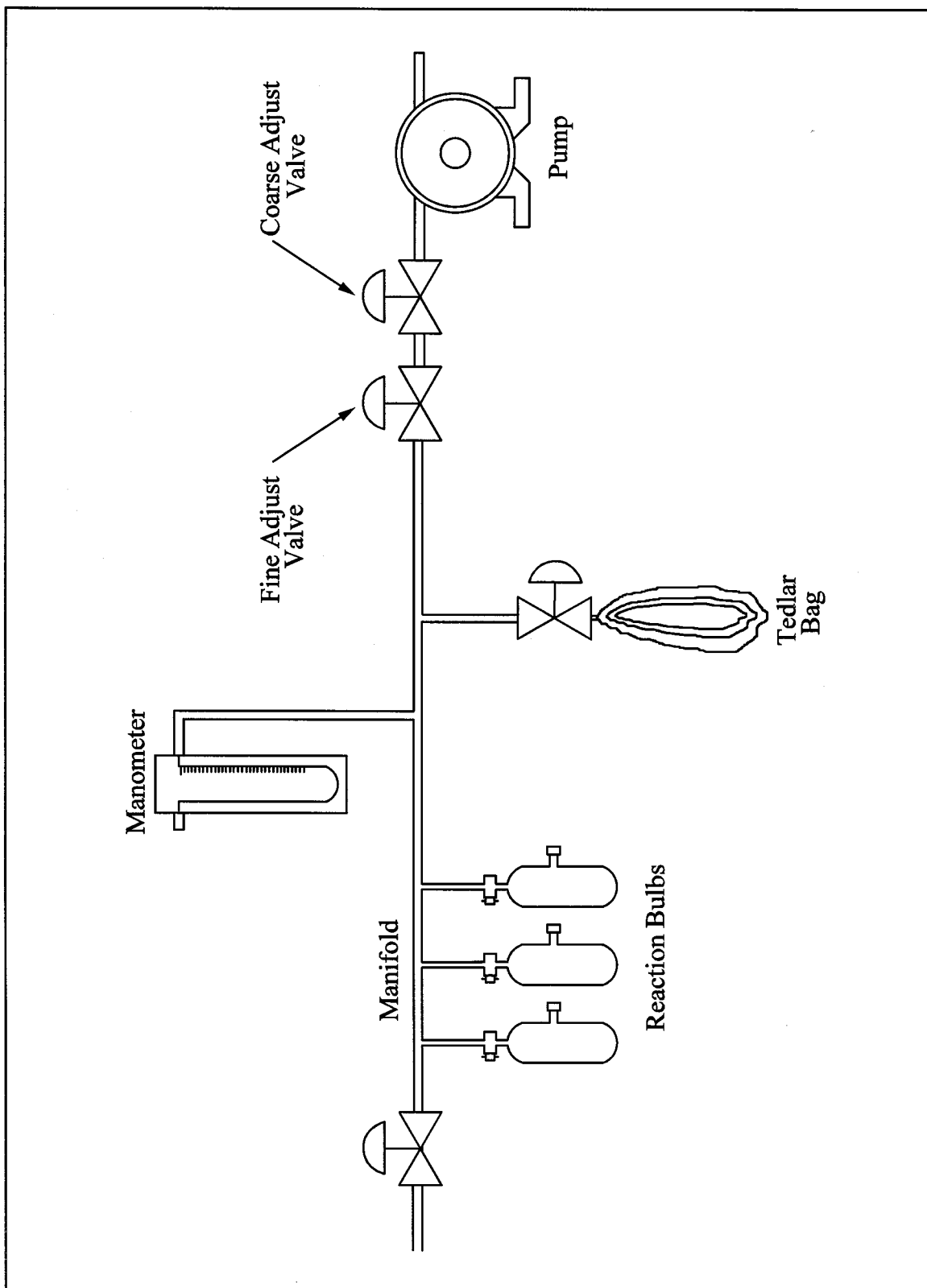


Figure 10A-3. Sample Bulb Filling System.

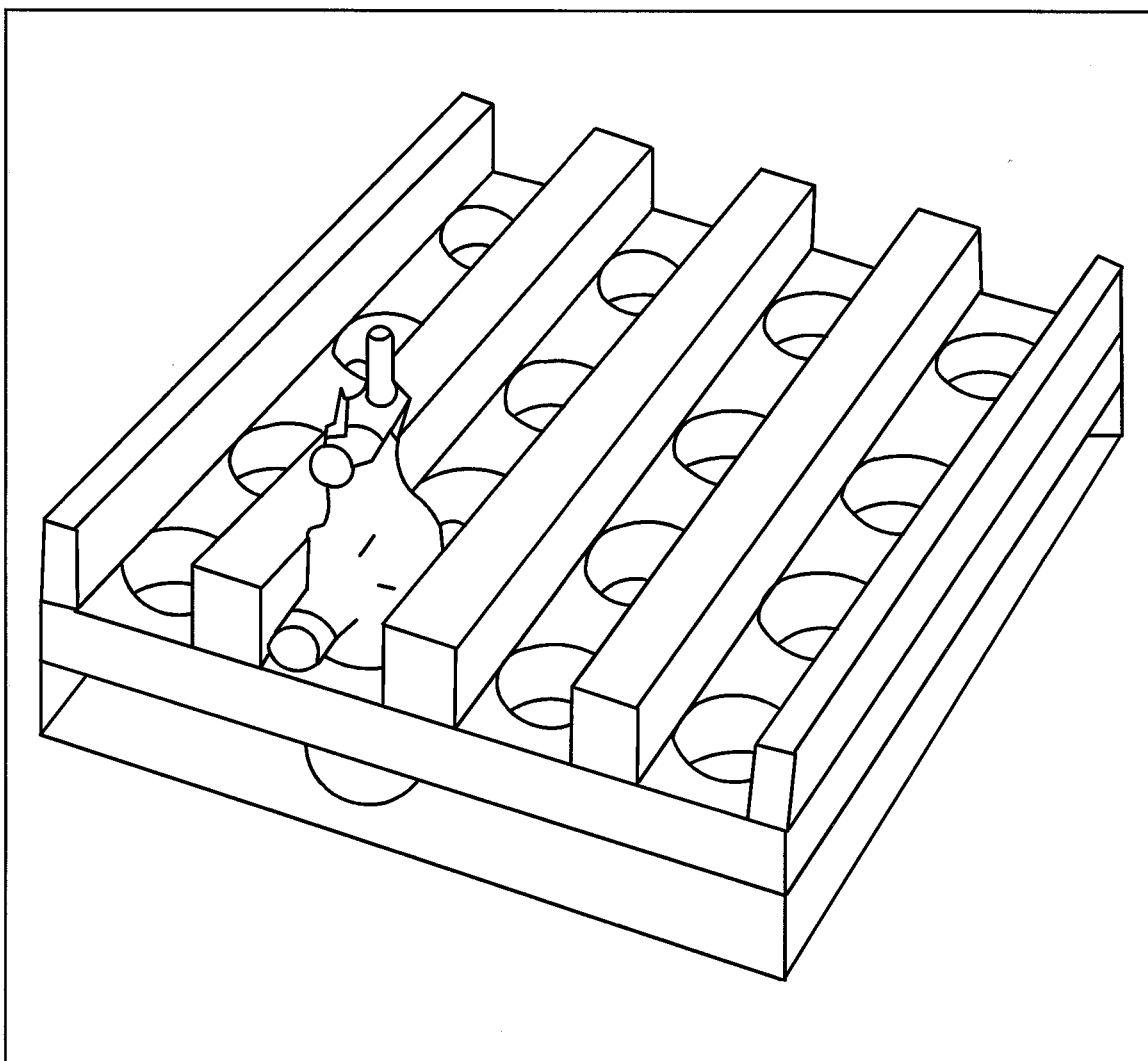


Figure 10A-4. Shaker Table Adapter.

BILLING CODE 6560-50-C

**Method 10B—Determination of Carbon Monoxide Emissions From Stationary Sources**

**Note:** This method is not inclusive with respect to specifications (e.g., equipment and

supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test

methods: Method 1, Method 4, Method 10A, and Method 25.

**1.0 Scope and Application**

**1.1 Analytes.**

Analyte	CAS No.	Sensitivity
Carbon monoxide (CO) .....	630-08-0	Not determined.

**1.2 Applicability.** This method applies to the measurement of CO emissions at petroleum refineries and from other sources when specified in an applicable subpart of the regulations.

**1.3 Data Quality Objectives.** Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

**2.0 Summary of Method**

**2.1** An integrated gas sample is extracted from the sampling point, passed through a conditioning system to remove interferences, and collected in a Tedlar bag. The CO is separated from the sample by gas chromatography (GC) and catalytically reduced to methane (CH<sub>4</sub>) which is determined by flame ionization detection (FID). The analytical portion of this method is

identical to applicable sections in Method 25 detailing CO measurement.

**3.0 Definitions. [Reserved]**

**4.0 Interferences**

**4.1** Carbon dioxide (CO<sub>2</sub>) and organics potentially can interfere with the analysis. Most of the CO<sub>2</sub> is removed from the sample by the alkaline permanganate conditioning system; any

residual CO<sub>2</sub> and organics are separated from the CO by GC.

### 5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions concerning the analytical procedure.

### 6.0 Equipment and Supplies

6.1 Sample Collection. Same as in Method 10A, Section 6.1.

6.2 Sample Analysis. A GC/FID analyzer, capable of quantifying CO in the sample and consisting of at least the following major components, is required for sample analysis. [Alternatively, complete Method 25 analytical systems

(Method 25, Section 6.3) are acceptable alternatives when calibrated for CO and operated in accordance with the Method 25 analytical procedures (Method 25, Section 11.0).]

6.2.1 Separation Column. A column capable of separating CO from CO<sub>2</sub> and organic compounds that may be present. A 3.2-mm (1/8-in.) OD stainless steel column packed with 1.7 m (5.5 ft.) of 60/80 mesh Carbosieve S-II (available from Supelco) has been used successfully for this purpose.

6.2.2 Reduction Catalyst. Same as in Method 25, Section 6.3.1.2.

6.2.3 Sample Injection System. Same as in Method 25, Section 6.3.1.4, equipped to accept a sample line from the Tedlar bag.

6.2.4 Flame Ionization Detector. Meeting the linearity specifications of Section 10.3 and having a minimal instrument range of 10 to 1,000 ppm CO.

6.2.5 Data Recording System. Analog strip chart recorder or digital integration system, compatible with the FID, for

permanently recording the analytical results.

### 7.0 Reagents and Standards

7.1 Sample Collection. Same as in Method 10A, Section 7.1.

7.2 Sample Analysis.

7.2.1 Carrier, Fuel, and Combustion Gases. Same as in Method 25, Sections 7.2.1, 7.2.2, and 7.2.3, respectively.

7.2.2 Calibration Gases. Three standard gases with nominal CO concentrations of 20, 200, and 1,000 ppm CO in nitrogen. The calibration gases shall be certified by the manufacturer to be  $\pm 2$  percent of the specified concentrations.

7.2.3 Reduction Catalyst Efficiency Check Calibration Gas. Standard CH<sub>4</sub> gas with a nominal concentration of 1,000 ppm in air.

### 8.0 Sample Collection, Preservation, Storage, and Transport

Same as in Method 10A, Section 8.0.

### 9.0 Quality Control

Section	Quality control measure	Effect
8.0 .....	Sample bag/sampling system leak-checks .....	Ensures that negative bias introduced through leakage is minimized.
10.1 .....	Carrier gas blank check .....	Ensures that positive bias introduced by contamination of carrier gas is less than 5 ppmv.
10.2 .....	Reduction catalyst efficiency check .....	Ensures that negative bias introduced by inefficient reduction catalyst is less than 5 percent.
10.3 .....	Analyzer calibration .....	Ensures linearity of analyzer response to standards.
11.2 .....	Triplicate sample analyses .....	Ensures precision of analytical results.

### 10.0 Calibration and Standardization

10.1 Carrier Gas Blank Check. Analyze each new tank of carrier gas with the GC analyzer according to Section 11.2 to check for contamination. The corresponding concentration must be less than 5 ppm for the tank to be acceptable for use.

10.2 Reduction Catalyst Efficiency Check. Prior to initial use, the reduction catalyst shall be tested for reduction efficiency. With the heated reduction catalyst bypassed, make triplicate injections of the 1,000 ppm CH<sub>4</sub> gas (Section 7.2.3) to calibrate the analyzer. Repeat the procedure using 1,000 ppm CO gas (Section 7.2.2) with the catalyst in operation. The reduction catalyst operation is acceptable if the CO response is within 5 percent of the certified gas value.

10.3 Analyzer Calibration. Perform this test before the system is first placed into operation. With the reduction catalyst in operation, conduct a linearity check of the analyzer using the standards specified in Section 7.2.2. Make triplicate injections of each calibration gas, and then calculate the average response factor (area/ppm) for

each gas, as well as the overall mean of the response factor values. The instrument linearity is acceptable if the average response factor of each calibration gas is within 2.5 percent of the overall mean value and if the relative standard deviation (calculated in Section 12.8 of Method 25) for each set of triplicate injections is less than 2 percent. Record the overall mean of the response factor values as the calibration response factor (R).

### 11.0 Analytical Procedure

11.1 Preparation for Analysis. Before putting the GC analyzer into routine operation, conduct the calibration procedures listed in Section 10.0. Establish an appropriate carrier flow rate and detector temperature for the specific instrument used.

11.2 Sample Analysis. Purge the sample loop with sample, and then inject the sample. Analyze each sample in triplicate, and calculate the average sample area (A). Determine the bag CO concentration according to Section 12.2.

### 12.0 Calculations and Data Analysis

Carry out calculations retaining at least one extra significant figure beyond that of the acquired data. Round off results only after the final calculation.

#### 12.1 Nomenclature.

A = Average sample area.

B<sub>w</sub> = Moisture content in the bag sample, fraction.

C = CO concentration in the stack gas, dry basis, ppm.

C<sub>b</sub> = CO concentration in the bag sample, dry basis, ppm.

F = Volume fraction of CO<sub>2</sub> in the stack, fraction.

P<sub>bar</sub> = Barometric pressure, mm Hg.

P<sub>w</sub> = Vapor pressure of the H<sub>2</sub>O in the bag (from Table 10A-2, Method 10A), mm Hg.

R = Mean calibration response factor, area/ppm.

12.2 CO Concentration in the Bag. Calculate C<sub>b</sub> using Equations 10B-1 and 10B-2. If condensate is visible in the Tedlar bag, calculate B<sub>w</sub> using Table 10A-2 of Method 10A and the temperature and barometric pressure in the analysis room. If condensate is not visible, calculate B<sub>w</sub> using the

temperature and barometric pressure at the sampling site.

$$B_w = \frac{P_w}{P_{\text{bar}}} \quad \text{Eq. 10B-1}$$

$$C_b = \frac{A}{R(1 - B_w)} \quad \text{Eq. 10B-2}$$

### 12.3 CO Concentration in the Stack

$$C = C_b(1 - F) \quad \text{Eq. 10B-3}$$

13.0 *Method Performance. [Reserved]*

14.0 *Pollution Prevention. [Reserved]*

15.0 *Waste Management. [Reserved]*

16.0 *References*

Same as in Method 25, Section 16.0, with the addition of the following:

1. Butler, F.E, J.E. Knoll, and M.R. Midgett. Development and Evaluation of Methods for Determining Carbon Monoxide Emissions.

Quality Assurance Division, Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC. June 1985. 33 pp.

17.0 *Tables, Diagrams, Flowcharts, and Validation Data. [Reserved]*

### **Method 11—Determination of Hydrogen Sulfide Content of Fuel Gas Streams in Petroleum Refineries**

#### 1.0 *Scope and Application*

##### 1.1 Analytes.

Analyte	CAS No.	Sensitivity
Hydrogen sulfide (H <sub>2</sub> S) .....	7783-06-4	8 mg/m <sup>3</sup> —740 mg/m <sup>3</sup> , (6 ppm—520 ppm).

1.2 *Applicability.* This method is applicable for the determination of the H<sub>2</sub>S content of fuel gas streams at petroleum refineries.

1.3 *Data Quality Objectives.* Adherence to the requirements of this method will enhance the quality of the

data obtained from air pollutant sampling methods.

#### 2.0 *Summary of Method*

2.1 A sample is extracted from a source and passed through a series of midget impingers containing a cadmium

sulfate (CdSO<sub>4</sub>) solution; H<sub>2</sub>S is absorbed, forming cadmium sulfide (CdS). The latter compound is then measured iodometrically.

#### 3.0 *Definitions. [Reserved]*

#### 4.0 Interferences

4.1 Any compound that reduces iodine ( $I_2$ ) or oxidizes the iodide ion will interfere in this procedure, provided it is collected in the  $CdSO_4$  impingers. Sulfur dioxide in concentrations of up to  $2,600\text{ mg/m}^3$  is removed with an impinger containing a hydrogen peroxide ( $H_2O_2$ ) solution. Thiols precipitate with  $H_2S$ . In the absence of  $H_2S$ , only traces of thiols are collected. When methane- and ethane-thiols at a total level of  $300\text{ mg/m}^3$  are present in addition to  $H_2S$ , the results vary from 2 percent low at an  $H_2S$  concentration of  $400\text{ mg/m}^3$  to 14 percent high at an  $H_2S$  concentration of  $100\text{ mg/m}^3$ . Carbonyl sulfide at a concentration of 20 percent does not interfere. Certain carbonyl-containing compounds react with iodine and produce recurring end points. However, acetaldehyde and acetone at concentrations of 1 and 3 percent, respectively, do not interfere.

4.2 Entrained  $H_2O_2$  produces a negative interference equivalent to 100 percent of that of an equimolar quantity of  $H_2S$ . Avoid the ejection of  $H_2O_2$  into the  $CdSO_4$  impingers.

#### 5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide. Irritating to eyes, skin, nose, and lungs. 30%  $H_2O_2$  is a strong oxidizing agent. Avoid contact with skin, eyes, and combustible material. Wear gloves when handling.

5.2.2 Hydrochloric Acid. Highly toxic. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent can be lethal in minutes. Will react with metals, producing hydrogen.

#### 6.0 Equipment and Supplies

6.1 Sample Collection. The following items are needed for sample collection:

6.1.1 Sampling Line. Teflon tubing, 6- to 7- mm ( $\frac{1}{4}$ -in.) ID, to connect the sampling train to the sampling valve.

6.1.2 Impingers. Five midjet impingers, each with 30-ml capacity. The internal diameter of the impinger tip must be  $1\text{ mm} \pm 0.05\text{ mm}$ . The impinger tip must be positioned 4 to 6 mm from the bottom of the impinger.

6.1.3 Tubing. Glass or Teflon connecting tubing for the impingers.

6.1.4 Ice Water Bath. To maintain absorbing solution at a low temperature.

6.1.5 Drying Tube. Tube packed with 6- to 16- mesh indicating-type

silica gel, or equivalent, to dry the gas sample and protect the meter and pump. If the silica gel has been used previously, dry at  $175^\circ\text{C}$  ( $350^\circ\text{F}$ ) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to approval of the Administrator.

**Note:** Do not use more than 30 g of silica gel. Silica gel adsorbs gases such as propane from the fuel gas stream, and use of excessive amounts of silica gel could result in errors in the determination of sample volume.

6.1.6 Sampling Valve. Needle valve, or equivalent, to adjust gas flow rate. Stainless steel or other corrosion-resistant material.

6.1.7 Volume Meter. Dry gas meter (DGM), sufficiently accurate to measure the sample volume within 2 percent, calibrated at the selected flow rate (about  $1.0\text{ liter/min}$ ) and conditions actually encountered during sampling. The meter shall be equipped with a temperature sensor (dial thermometer or equivalent) capable of measuring temperature to within  $3^\circ\text{C}$  ( $5.4^\circ\text{F}$ ). The gas meter should have a petcock, or equivalent, on the outlet connector which can be closed during the leak-check. Gas volume for one revolution of the meter must not be more than 10 liters.

6.1.8 Rate Meter. Rotameter, or equivalent, to measure flow rates in the range from 0.5 to 2 liters/min ( $1\text{ to }4\text{ ft}^3/\text{hr}$ ).

6.1.9 Graduated Cylinder. 25-ml size.

6.1.10 Barometer. Mercury, aneroid, or other barometer capable of measuring

atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby National Weather Service station, in which case, the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and the sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in Hg) per 30 m (100 ft) elevation increase or vice-versa for elevation decrease.

6.1.11 U-tube Manometer. 0-; to 30-cm water column, for leak-check procedure.

6.1.12 Rubber Squeeze Bulb. To pressurize train for leak-check.

6.1.13 Tee, Pinchclamp, and Connecting Tubing. For leak-check.

6.1.14 Pump. Diaphragm pump, or equivalent. Insert a small surge tank between the pump and rate meter to minimize the pulsation effect of the diaphragm pump on the rate meter. The pump is used for the air purge at the end of the sample run; the pump is not ordinarily used during sampling, because fuel gas streams are usually sufficiently pressurized to force sample gas through the train at the required flow rate. The pump need not be leak-free unless it is used for sampling.

6.1.15 Needle Valve or Critical Orifice. To set air purge flow to 1 liter/min.

6.1.16 Tube Packed with Active Carbon. To filter air during purge.

6.1.17 Volumetric Flask. One 1000-ml.

6.1.18 Volumetric Pipette. One 15-ml.

6.1.19 Pressure-Reduction Regulator. Depending on the sampling stream pressure, a pressure-reduction regulator may be needed to reduce the pressure of the gas stream entering the Teflon sample line to a safe level.

6.1.20 Cold Trap. If condensed water or amine is present in the sample stream, a corrosion-resistant cold trap shall be used immediately after the sample tap. The trap shall not be operated below 0 °C (32 °F) to avoid condensation of C<sub>3</sub> or C<sub>4</sub> hydrocarbons.

6.2 Sample Recovery. The following items are needed for sample recovery:

6.2.1 Sample Container. Iodine flask, glass-stoppered, 500-ml size.

6.2.2 Volumetric Pipette. One 50-ml.

6.2.3 Graduated Cylinders. One each 25- and 250-ml.

6.2.4 Erlenmeyer Flasks. 125-ml.

6.2.5 Wash Bottle.

6.2.6 Volumetric Flasks. Three 1000-ml.

6.3 Sample Analysis. The following items are needed for sample analysis:

6.3.1 Flask. Glass-stoppered iodine flask, 500-ml.

6.3.2 Burette. 50-ml.

6.3.3 Erlenmeyer Flask. 125-ml.

6.3.4 Volumetric Pipettes. One 25-ml; two each 50- and 100-ml.

6.3.5 Volumetric Flasks. One 1000-ml; two 500-ml.

6.3.6 Graduated Cylinders. One each 10- and 100-ml.

## 7.0 Reagents and Standards

**Note:** Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 CdSO<sub>4</sub> Absorbing Solution. Dissolve 41 g of 3CdSO<sub>4</sub>·8H<sub>2</sub>O and 15 ml of 0.1 M sulfuric acid in a 1-liter volumetric flask that contains approximately ¾ liter of water. Dilute to volume with deionized, distilled water. Mix thoroughly. The pH should be 3 ± 0.1. Add 10 drops of Dow-Corning Antifoam B. Shake well before use. This solution is stable for at least one month. If Antifoam B is not used, a more labor-intensive sample recovery procedure is required (see Section 11.2).

7.1.2 Hydrogen Peroxide, 3 Percent. Dilute 30 percent H<sub>2</sub>O<sub>2</sub> to 3 percent as needed. Prepare fresh daily.

7.1.3 Water. Deionized distilled to conform to ASTM D 1193-77 or 91, Type 3 (incorporated by reference—see § 60.17). The KMnO<sub>4</sub> test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.2 Sample Recovery. The following reagents are needed for sample recovery:

7.2.1 Water. Same as Section 7.1.3.

7.2.2 Hydrochloric Acid (HCl) Solution, 3 M. Add 240 ml of concentrated HCl (specific gravity 1.19) to 500 ml of water in a 1-liter volumetric flask. Dilute to 1 liter with water. Mix thoroughly.

7.2.3 Iodine (I<sub>2</sub>) Solution, 0.1 N. Dissolve 24 g of potassium iodide (KI) in 30 ml of water. Add 12.7 g of resublimed iodine (I<sub>2</sub>) to the KI solution. Shake the mixture until the I<sub>2</sub> is completely dissolved. If possible, let the solution stand overnight in the dark. Slowly dilute the solution to 1 liter with water, with swirling. Filter the solution if it is cloudy. Store solution in a brown-glass reagent bottle.

7.2.4 Standard I<sub>2</sub> Solution, 0.01 N. Pipette 100.0 ml of the 0.1 N iodine solution into a 1-liter volumetric flask, and dilute to volume with water. Standardize daily as in Section 10.2.1. This solution must be protected from

light. Reagent bottles and flasks must be kept tightly stoppered.

7.3 Sample Analysis. The following reagents and standards are needed for sample analysis:

7.3.1 Water. Same as in Section

7.1.3.

7.3.2 Standard Sodium Thiosulfate Solution, 0.1 N. Dissolve 24.8 g of sodium thiosulfate pentahydrate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O) or 15.8 g of anhydrous sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) in 1 liter of water, and add 0.01 g of anhydrous sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) and 0.4 ml of chloroform (CHCl<sub>3</sub>) to stabilize. Mix thoroughly by shaking or by aerating with nitrogen for approximately 15 minutes, and store in a glass-stoppered, reagent bottle. Standardize as in Section 10.2.2.

7.3.3 Standard Sodium Thiosulfate Solution, 0.01 N. Pipette 50.0 ml of the standard 0.1 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution into a volumetric flask, and dilute to 500 ml with water.

**Note:** A 0.01 N phenylarsine oxide (C<sub>6</sub>H<sub>5</sub>AsO) solution may be prepared instead of 0.01 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (see Section 7.3.4).

7.3.4 Standard Phenylarsine Oxide Solution, 0.01 N. Dissolve 1.80 g of (C<sub>6</sub>H<sub>5</sub>AsO) in 150 ml of 0.3 N sodium hydroxide. After settling, decant 140 ml of this solution into 800 ml of water. Bring the solution to pH 6-7 with 6 N HCl, and dilute to 1 liter with water. Standardize as in Section 10.2.3.

7.3.5 Starch Indicator Solution. Suspend 10 g of soluble starch in 100 ml of water, and add 15 g of potassium hydroxide (KOH) pellets. Stir until dissolved, dilute with 900 ml of water, and let stand for 1 hour. Neutralize the alkali with concentrated HCl, using an indicator paper similar to Alkacid test ribbon, then add 2 ml of glacial acetic acid as a preservative.

**Note:** Test starch indicator solution for decomposition by titrating with 0.01 N I<sub>2</sub> solution, 4 ml of starch solution in 200 ml of water that contains 1 g of KI. If more than 4 drops of the 0.01 N I<sub>2</sub> solution are required to obtain the blue color, a fresh solution must be prepared.

## 8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling Train Preparation. Assemble the sampling train as shown in Figure 11-1, connecting the five midjet impingers in series. Place 15 ml of 3 percent H<sub>2</sub>O<sub>2</sub> solution in the first impinger. Leave the second impinger empty. Place 15 ml of the CdSO<sub>4</sub> solution in the third, fourth, and fifth impingers. Place the impinger assembly in an ice water bath container, and place water and crushed ice around the impingers. Add more ice during the run, if needed.

## 8.2 Leak-Check Procedure.

8.2.1 Connect the rubber bulb and manometer to the first impinger, as shown in Figure 11–1. Close the petcock on the DGM outlet. Pressurize the train to 25 cm water with the bulb, and close off the tubing connected to the rubber bulb. The train must hold 25 cm water pressure with not more than a 1 cm drop in pressure in a 1-minute interval. Stopcock grease is acceptable for sealing ground glass joints.

8.2.2 If the pump is used for sampling, it is recommended, but not required, that the pump be leak-checked separately, either prior to or after the sampling run. To leak-check the pump, proceed as follows: Disconnect the drying tube from the impinger assembly. Place a vacuum gauge at the inlet to either the drying tube or the pump, pull a vacuum of 250 mm Hg (10 in. Hg), plug or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum should remain stable for at least 30 seconds. If performed prior to the sampling run, the pump leak-check

should precede the leak-check of the sampling train described immediately above; if performed after the sampling run, the pump leak-check should follow the sampling train leak-check.

8.3 Purge the connecting line between the sampling valve and the first impinger by disconnecting the line from the first impinger, opening the sampling valve, and allowing process gas to flow through the line for one to two minutes. Then, close the sampling valve, and reconnect the line to the impinger train. Open the petcock on the dry gas meter outlet. Record the initial DGM reading.

8.4 Open the sampling valve, and then adjust the valve to obtain a rate of approximately 1 liter/min (0.035 cfm). Maintain a constant ( $\pm 10$  percent) flow rate during the test. Record the DGM temperature.

8.5 Sample for at least 10 minutes. At the end of the sampling time, close the sampling valve, and record the final volume and temperature readings. Conduct a leak-check as described in Section 8.2 above.

8.6 Disconnect the impinger train from the sampling line. Connect the charcoal tube and the pump as shown in Figure 11–1. Purge the train [at a rate of 1 liter/min (0.035 ft<sup>3</sup>/min)] with clean ambient air for 15 minutes to ensure that all H<sub>2</sub>S is removed from the H<sub>2</sub>O<sub>2</sub>. For sample recovery, cap the open ends, and remove the impinger train to a clean area that is away from sources of heat. The area should be well lighted, but not exposed to direct sunlight.

## 8.7 Sample Recovery.

8.7.1 Discard the contents of the H<sub>2</sub>O<sub>2</sub> impinger. Carefully rinse with water the contents of the third, fourth, and fifth impingers into a 500-ml iodine flask.

**Note:** The impingers normally have only a thin film of CdS remaining after a water rinse. If Antifoam B was not used or if significant quantities of yellow CdS remain in the impingers, the alternative recovery procedure in Section 11.2 must be used.

8.7.2 Proceed to Section 11 for the analysis.

## 9.0 Quality Control

Section	Quality control measure	Effect
8.2, 10.1 .....	Sampling equipment leak-check and calibration .....	Ensure accurate measurement of sample volume.
11.2 .....	Replicate titrations of blanks .....	Ensure precision of titration determinations.

## 10.0 Calibration and Standardization

**Note:** Maintain a log of all calibrations.

10.1 Calibration. Calibrate the sample collection equipment as follows.

### 10.1.1 Dry Gas Meter.

10.1.1.1 Initial Calibration. The DGM shall be calibrated before its initial use in the field. Proceed as follows: First, assemble the following components in series: Drying tube, needle valve, pump, rotameter, and DGM. Then, leak-check the metering system as follows: Place a vacuum gauge (at least 760 mm Hg) at the inlet to the drying tube, and pull a vacuum of 250 mm Hg (10 in. Hg); plug or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum shall remain stable for at least 30 seconds. Carefully release the vacuum gauge before releasing the flow meter end. Next, calibrate the DGM (at the sampling flow rate specified by the method) as follows: Connect an appropriately sized wet-test meter (e.g., 1 liter per revolution) to the inlet of the drying tube. Make three independent calibration runs, using at least five revolutions of the DGM per run. Calculate the calibration factor, Y (wet-test meter calibration volume divided by the DGM volume, both volumes adjusted to the same reference temperature and pressure), for each run,

and average the results. If any Y value deviates by more than 2 percent from the average, the DGM is unacceptable for use. Otherwise, use the average as the calibration factor for subsequent test runs.

10.1.1.2 Post-Test Calibration Check. After each field test series, conduct a calibration check as in Section 10.1.1.1, above, except for the following two variations: (a) three or more revolutions of the DGM may be used and (b) only two independent runs need be made. If the calibration factor does not deviate by more than 5 percent from the initial calibration factor (determined in Section 10.1.1.1), then the DGM volumes obtained during the test series are acceptable. If the calibration factor deviates by more than 5 percent, recalibrate the DGM as in Section 10.1.1.1, and for the calculations, use the calibration factor (initial or recalibration) that yields the lower gas volume for each test run.

10.1.2 Temperature Sensors. Calibrate against mercury-in-glass thermometers.

10.1.3 Rate Meter. The rate meter need not be calibrated, but should be cleaned and maintained according to the manufacturer's instructions.

10.1.4 Barometer. Calibrate against a mercury barometer.

### 10.2 Standardization.

#### 10.2.1 Iodine Solution

Standardization. Standardize the 0.01 N I<sub>2</sub> solution daily as follows: Pipette 25 ml of the I<sub>2</sub> solution into a 125-ml Erlenmeyer flask. Add 2 ml of 3 M HCl. Titrate rapidly with standard 0.01 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution or with 0.01 N C<sub>6</sub>H<sub>5</sub>AsO until the solution is light yellow, using gentle mixing. Add four drops of starch indicator solution, and continue titrating slowly until the blue color just disappears. Record the volume of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution used, V<sub>SI</sub>, or the volume of C<sub>6</sub>H<sub>5</sub>AsO solution used, V<sub>AI</sub>, in ml. Repeat until replicate values agree within 0.05 ml. Average the replicate titration values which agree within 0.05 ml, and calculate the exact normality of the I<sub>2</sub> solution using Equation 11–3. Repeat the standardization daily.

10.2.2 Sodium Thiosulfate Solution Standardization. Standardize the 0.1 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution as follows: Oven-dry potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) at 180 to 200 °C (360 to 390 °F). To the nearest milligram, weigh 2 g of the dichromate (W). Transfer the dichromate to a 500-ml volumetric flask, dissolve in water, and dilute to exactly 500 ml. In a 500-ml iodine flask, dissolve approximately 3 g of KI in 45 ml of water, then add 10 ml of 3 M HCl solution. Pipette 50



ml of the dichromate solution into this mixture. Gently swirl the contents of the flask once, and allow it to stand in the dark for 5 minutes. Dilute the solution with 100 to 200 ml of water, washing down the sides of the flask with part of the water. Titrate with 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  until the solution is light yellow. Add 4 ml of starch indicator and continue titrating slowly to a green end point. Record the volume of  $\text{Na}_2\text{S}_2\text{O}_3$  solution used,  $V_S$ , in ml. Repeat until replicate values agree within 0.05 ml. Calculate the normality using Equation 11-1. Repeat the standardization each week or after each test series, whichever time is shorter.

**10.2.3 Phenylarsine Oxide Solution Standardization.** Standardize the 0.01 N  $\text{C}_6\text{H}_5\text{AsO}$  (if applicable) as follows: Oven-dry  $\text{K}_2\text{Cr}_2\text{O}_7$  at 180 to 200 °C (360 to 390 °F). To the nearest milligram, weigh 2 g of the dichromate (W). Transfer the dichromate to a 500-ml volumetric flask, dissolve in water, and dilute to exactly 500 ml. In a 500-ml iodine flask, dissolve approximately 0.3 g of KI in 45 ml of water, then add 10 ml of 3 M HCl. Pipette 5 ml of the dichromate solution into the iodine flask. Gently swirl the contents of the flask once, and allow it to stand in the dark for 5 minutes. Dilute the solution with 100 to 200 ml of water, washing down the sides of the flask with part of the water. Titrate with 0.01 N  $\text{C}_6\text{H}_5\text{AsO}$  until the solution is light yellow. Add 4 ml of starch indicator, and continue titrating slowly to a green end point. Record the volume of  $\text{C}_6\text{H}_5\text{AsO}$  used,  $V_A$ , in ml. Repeat until replicate analyses agree within 0.05 ml. Calculate the normality using Equation 11-2. Repeat the standardization each week or after each test series, whichever time is shorter.

#### 11.0 Analytical Procedure

Conduct the titration analyses in a clean area away from direct sunlight.

**11.1** Pipette exactly 50 ml of 0.01 N  $\text{I}_2$  solution into a 125-ml Erlenmeyer flask. Add 10 ml of 3 M HCl to the solution. Quantitatively rinse the acidified  $\text{I}_2$  into the iodine flask. Stopper the flask immediately, and shake briefly.

**11.2** Use these alternative procedures if Antifoam B was not used or if significant quantities of yellow CdS remain in the impingers. Extract the remaining CdS from the third, fourth, and fifth impingers using the acidified  $\text{I}_2$  solution. Immediately after pouring the acidified  $\text{I}_2$  into an impinger, stopper it and shake for a few moments, then transfer the liquid to the iodine flask. Do not transfer any rinse portion from one impinger to another; transfer it

directly to the iodine flask. Once the acidified  $\text{I}_2$  solution has been poured into any glassware containing CdS, the container must be tightly stoppered at all times except when adding more solution, and this must be done as quickly and carefully as possible. After adding any acidified  $\text{I}_2$  solution to the iodine flask, allow a few minutes for absorption of the  $\text{H}_2\text{S}$  before adding any further rinses. Repeat the  $\text{I}_2$  extraction until all CdS is removed from the impingers. Extract that part of the connecting glassware that contains visible CdS. Quantitatively rinse all the  $\text{I}_2$  from the impingers, connectors, and the beaker into the iodine flask using water. Stopper the flask and shake briefly.

**11.3** Allow the iodine flask to stand about 30 minutes in the dark for absorption of the  $\text{H}_2\text{S}$  into the  $\text{I}_2$ , then complete the titration analysis as outlined in Sections 11.5 and 11.6.

**Note:** Iodine evaporates from acidified  $\text{I}_2$  solutions. Samples to which acidified  $\text{I}_2$  has been added may not be stored, but must be analyzed in the time schedule stated above.

**11.4** Prepare a blank by adding 45 ml of  $\text{CdSO}_4$  absorbing solution to an iodine flask. Pipette exactly 50 ml of 0.01 N  $\text{I}_2$  solution into a 125-ml Erlenmeyer flask. Add 10 ml of 3 M HCl. Stopper the flask, shake briefly, let stand 30 minutes in the dark, and titrate with the samples.

**Note:** The blank must be handled by exactly the same procedure as that used for the samples.

**11.5** Using 0.01 N  $\text{Na}_2\text{S}_2\text{O}_3$  solution (or 0.01 N  $\text{C}_6\text{H}_5\text{AsO}$ , if applicable), rapidly titrate each sample in an iodine flask using gentle mixing, until solution is light yellow. Add 4 ml of starch indicator solution, and continue titrating slowly until the blue color just disappears. Record the volume of  $\text{Na}_2\text{S}_2\text{O}_3$  solution used,  $V_{TT}$ , or the volume of  $\text{C}_6\text{H}_5\text{AsO}$  solution used,  $V_{AT}$ , in ml.

**11.6** Titrate the blanks in the same manner as the samples. Run blanks each day until replicate values agree within 0.05 ml. Average the replicate titration values which agree within 0.05 ml.

#### 12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures only after the final calculation.

##### 12.1 Nomenclature.

$C_{\text{H}_2\text{S}}$  = Concentration of  $\text{H}_2\text{S}$  at standard conditions, mg/dscm.

$N_A$  = Normality of standard  $\text{C}_6\text{H}_5\text{AsO}$  solution, g-eq/liter.

$N_I$  = Normality of standard  $\text{I}_2$  solution, g-eq/liter.

$N_S$  = Normality of standard ( $\approx 0.1$  N)

$\text{Na}_2\text{S}_2\text{O}_3$  solution, g-eq/liter.

$N_T$  = Normality of standard ( $\approx 0.01$  N)

$\text{Na}_2\text{S}_2\text{O}_3$  solution, assumed to be 0.1 N, g-eq/liter.

$P_{\text{bar}}$  = Barometric pressure at the sampling site, mm Hg.

$P_{\text{std}}$  = Standard absolute pressure, 760 mm Hg.

$T_m$  = Average DGM temperature, °K.

$T_{\text{std}}$  = Standard absolute temperature, 293 °K.

$V_A$  = Volume of  $\text{C}_6\text{H}_5\text{AsO}$  solution used for standardization, ml.

$V_{AI}$  = Volume of standard  $\text{C}_6\text{H}_5\text{AsO}$  solution used for titration analysis, ml.

$V_I$  = Volume of standard  $\text{I}_2$  solution used for standardization, ml.

$V_{IT}$  = Volume of standard  $\text{I}_2$  solution used for titration analysis, normally 50 ml.

$V_m$  = Volume of gas sample at meter conditions, liters.

$V_{m(\text{std})}$  = Volume of gas sample at standard conditions, liters.

$V_{SI}$  = Volume of "0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  solution used for standardization, ml.

$V_T$  = Volume of standard ( $\approx 0.01$  N)  $\text{Na}_2\text{S}_2\text{O}_3$  solution used in standardizing iodine solution (see Section 10.2.1), ml.

$V_{TT}$  = Volume of standard ( $\approx 0.01$  N)  $\text{Na}_2\text{S}_2\text{O}_3$  solution used for titration analysis, ml.

$W$  = Weight of  $\text{K}_2\text{Cr}_2\text{O}_7$  used to standardize  $\text{Na}_2\text{S}_2\text{O}_3$  or  $\text{C}_6\text{H}_5\text{AsO}$  solutions, as applicable (see Sections 10.2.2 and 10.2.3), g.

$Y$  = DGM calibration factor.

**12.2 Normality of the Standard ( $\approx 0.1$  N) Sodium Thiosulfate Solution.**

$$N_S = \frac{2.039 W}{V_S} \quad \text{Eq. 11-1}$$

Where:

2.039 = Conversion factor  
= (6 g-eq  $\text{I}_2$ /mole  $\text{K}_2\text{Cr}_2\text{O}_7$ ) (1,000 ml/liter)/(294.2 g  $\text{K}_2\text{Cr}_2\text{O}_7$ /mole) (10 aliquot factor)

**12.3 Normality of Standard Phenylarsine Oxide Solution (if applicable).**

$$N_A = \frac{0.2039 W}{V_A} \quad \text{Eq. 11-2}$$

Where:

0.2039 = Conversion factor.  
= (6 g-eq  $\text{I}_2$ /mole  $\text{K}_2\text{Cr}_2\text{O}_7$ ) (1,000 ml/liter)/(294.2 g  $\text{K}_2\text{Cr}_2\text{O}_7$ /mole) (100 aliquot factor)

**12.4 Normality of Standard Iodine Solution.**

$$N_I = \frac{N_T V_T}{V_I} \quad \text{Eq. 11-3}$$

**Note:** If  $C_6H_5AsO$  is used instead of  $Na_2S_2O_3$ , replace  $N_T$  and  $V_T$  in Equation 11-3 with  $N_A$  and  $V_{AS}$ , respectively (see Sections 10.2.1 and 10.2.3).

12.5 Dry Gas Volume. Correct the sample volume measured by the DGM to

standard conditions (20 °C and 760 mm Hg).

$$V_{m(std)} = V_m Y \frac{T_{std}}{T_m} \frac{P_{bar}}{P_{std}} \quad \text{Eq. 11-4}$$

12.6 Concentration of  $H_2S$ . Calculate the concentration of  $H_2S$  in the gas stream at standard conditions using Equation 11-5:

$$C_{H_2S} = 17.04 \times 10^3 \frac{(V_{IT}N_I - V_{TT}N_T)_{sample} - (V_{IT}N_I - V_{TT}N_T)_{blank}}{V_{m(std)}} \quad \text{Eq. 11-5}$$

Where:

$17.04 \times 10^3$  = Conversion factor  
= (34.07 g/mole  $H_2S$ ) (1,000 liters/ $m^3$ )  
(1,000mg/g)/(1,000 ml/liter) ( $2H_2S$   
eq/mole)

**Note:** If  $C_6H_5AsO$  is used instead of  $Na_2S_2O_3$ , replace  $N_A$  and  $V_{AT}$  in Equation 11-5 with  $N_A$  and  $V_{AT}$ , respectively (see Sections 11.5 and 10.2.3).

### 13.0 Method Performance

13.1 Precision. Collaborative testing has shown the intra-laboratory precision to be 2.2 percent and the inter-laboratory precision to be 5 percent.

13.2 Bias. The method bias was shown to be -4.8 percent when only  $H_2S$  was present. In the presence of the

interferences cited in Section 4.0, the bias was positive at low  $H_2S$  concentration and negative at higher concentrations. At 230 mg  $H_2S/m^3$ , the level of the compliance standard, the bias was +2.7 percent. Thiols had no effect on the precision.

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

### 16.0 References

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